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A Study of the Mechanism of
Alkali Cellulose Autoxidation

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A STUDY OF THE MECHANISM OF
ALKALI CELLULOSE AUTOXIDATION

A thesis submitted by

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SUMMARY AND CONCLUSIONS

The generally accepted mechanism for the alkali cellulose autoxidation reaction is a free radical mechanism, first proposed in 1949 by Entwistle, Cole, and Wooding. No direct evidence for the existence of free radicals in the alkali cellulose system has ever been presented. The objective of the work in this research was to show to what extent free radicals are present in the autoxidizing alkali cellulose system, and whether or not free radicals are responsible for the reactions known to occur.

The Entwistle, Cole, and Wooding mechanism postulates the hydroxyl radical as an intermediate. This is known to react readily with aromatic substances to form phenols. If one assumes the mechanism, one would predict the following effects when aromatic substances are added to autoxidizing alkali cellulose.

First, phenolic substances should have been formed. Second, oxygen consumption should have been sharply reduced. Third, the degradation of alkali cellulose should have been inhibited. From the experimental results the following observations were made.

(a) No more than 0.36% of the predicted amount of phenol was produced when alkali cellulose was autoxidized in the presence of benzene.

(b) Neither benzoic acid nor 1-naphthalenesulfonic acid caused inhibition of the oxygen consumption of autoxidizing alkali cellulose.

(c) Neither benzene, benzoic acid nor 1-naphthalenesulfonic acid caused inhibition of the degradation process that occurs during alkali cellulose autoxidation.

Controls were conducted which demonstrated the stability of phenol in autoxidizing alkali cellulose and showed that phenol would have been formed from benzene and free hydroxyl radical.

From this, and other work, the following conclusions can be drawn:

1. The free hydroxyl radical is not an intermediate or a by-product of alkali cellulose autoxidation, unless it reacts much faster with cellulose than with benzene.
2. Phenol does not inhibit alkali cellulose autoxidation.
3. Alkali cellulose autoxidation is not catalyzed by visible light, although photocatalysis is characteristic of free radical autoxidations.
4. Electron paramagnetic resonance spectra of autoxidizing alkali cellulose fail to show any significant free radical responses.

Since none of the evidence obtained supports the free radical mechanism, an alternative mechanism has been postulated to account for the known facts of alkali cellulose autoxidation. The first step in this mechanism is a spontaneous reaction between oxygen and reducing groups causing formation of perhydroxyl ion. The perhydroxyl ion then reacts with cellulose at a new site, forming a linkage that is sensitive to alkaline degradation, thus causing both rupture and production of new reducing groups. The reaction is autocatalytic because more than one reducing group is formed during the complex alkaline degradation processes that follow peroxide attack.

INTRODUCTION

ALKALI CELLULOSE AUTOXIDATION

When cellulose is steeped in strong alkaline solution, then pressed to a state of apparent dryness (1 part cellulose to 2 parts alkali solution), it reacts slowly with atmospheric oxygen. This reaction is called alkali cellulose autoxidation. The uptake of oxygen is accompanied by random degradation of the cellulose molecule. It has been known for a long time that the presence of oxygen is necessary in order for degradation to occur (1, 77).

This reaction was encountered early in cellulose technology. From Schwalbe's (2) text we find that early workers on the mercerization process (78, 79) observed cellulose degradation when the cotton was allowed to remain in contact with strong alkali for long periods. In the late 1890's the reaction was first utilized as a means of lowering molecular weight of cellulose in the viscose process (3). This reaction, usually called "aging", is still an important step in the manufacture of viscose rayon.

There has been little real success in proposing a mechanism that explains all of the known facts of the reaction. The earlier theories of Davidson (4), Pacsu (5) and Heuser (6) were not very comprehensive, and have been given little consideration since Entwistle, Cole and Wooding (7) advanced a theory based on free radical intermediates in 1949. This theory, in general, explains how oxygen absorption may occur; the earlier theories were more concerned with chain rupture. The free radical theory seems to be quite well accepted today, but other workers, such as à Brassard (8), Müller (9), Urbigit (10) and Marraccini and Kleinert (11), have suggested that some other mechanism is involved in alkali cellulose autoxidation.

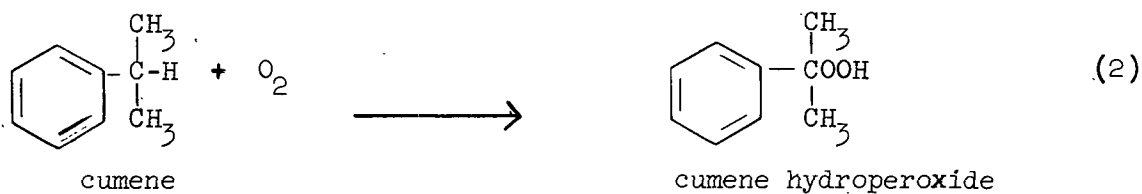
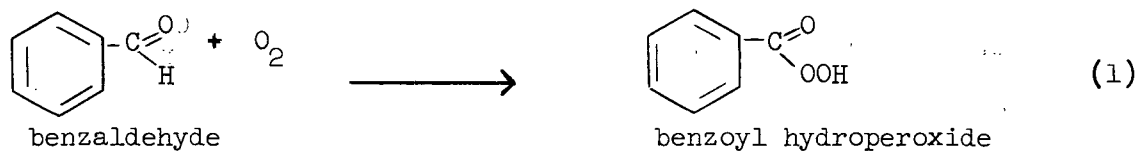
AUTOXIDATION IN GENERAL (12)

Many organic substances react spontaneously with oxygen at room temperature and atmospheric pressure. Benzaldehyde, tetralin and drying oils are common examples of such substances. This process has come to be known as autoxidation.

Transition metals usually act as positive catalysts, whereas phenols, particularly of the hydroquinone type, are strong inhibitors or "antioxidants". Many autoxidations are photocatalytic, showing very high quantum yields, 10,000 to 15,000 being common. It is quite evident that a chain reaction is operative in such cases.

The process of autoxidation is related to the chemical properties of oxygen and organic substances. The oxygen molecule is a diradical, with two unpaired electrons. Thus, although two electrons are needed to reduce the oxygen molecule to a peroxide, they need not be transferred as an electron pair, but can occur as two single electron transfers. It is not surprising, then, to discover that nearly all autoxidative reactions are explained in terms of free-radical intermediates.

Not all organic substances autoxidize with the same ease. In general, substances which have a hydrogen atom with a high electron density are susceptible to autoxidation. Such sites are found on tertiary carbon atoms or a benzylic C-H group. Allylic C-H bonds on olefins are easily autoxidized. Aldehydes autoxidize easily. If a compound possesses a combination of these structural characteristics, it usually has a very marked tendency to autoxidize. Examples such as benzaldehyde (both benzylic and an aldehyde) and cumene (both benzylic and tertiary placement) illustrate this phenomenon.



Hydroquinone and related substances autoxidize under alkaline conditions; these reactions produce hydrogen peroxide, and do so by virtue of the strongly reducing character of the hydroquinone anion. Esters, alcohols, acids, and simple phenols do not generally undergo autoxidation.

In brief, then it may be stated that an organic substance must possess some strongly reducing site for oxygen attack in order to be autoxidizable.

Another common feature of essentially all autoxidations is that they produce some kind of a peroxide as the product of the first step of the reaction with molecular oxygen. Molecular oxygen does not spontaneously dissociate into atoms under autoxidizing conditions, so it must pass through some peroxide intermediate before oxygen can be added to the organic substrate. In many cases, the peroxides can be recovered as a hydroperoxide or hydrogen peroxide in high yield; in other cases, the initial peroxide production is equal to the initial oxygen consumption but falls off with time, because the peroxides either decompose or react.

There are various mechanisms that account for different autoxidation reactions. However, it will be particularly instructive if we consider in detail the mechanism of a hydrocarbon autoxidation, for it is the most general and will illustrate a typical autoxidation (13 - 15). This is also the mechanism considered by Entwistle, Cole, and Wooding to be analogous to alkali cellulose autoxidation (7).

First of all, some kind of initiation reaction must occur to start the reaction sequence:

1. Initiation (a very slow reaction)



Then each of the radical species above can enter into a propagation chain, sometimes of great length:

2. Propagation (a fast reaction)



(Please note that this is a repetitive process.)

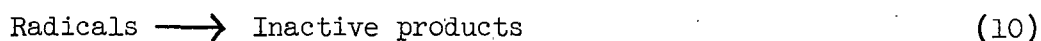
The above sequence would be enough to account for autoxidation if it were not for the fact that the reaction is usually autocatalytic. Addition of hydroperoxide speeds up the reaction. Therefore, an autocatalysis step must be occurring:

3. Autocatalysis



The rates of autocatalytic reactions usually reach some steady-state value, at which free radicals lost by terminations balance those produced by initiation and autocatalysis. These termination reactions are usually complex, and lead to a large variety of chemical by-products.

4. Termination



In the case of the reaction of hydrocarbons, this is an addition polymerization reaction, leading to the formation of resinous polymers.

It must be stressed at this point that there are many other autoxidation mechanisms than the one just described. Many autoxidation reactions are nonchain in nature. Some are even reversible to a large degree. Some reactions produce hydrogen peroxide and no organic hydroperoxide. Some involve organic anions, whereas others involve active hydrogen atoms. With such a wide range of mechanisms for different autoxidations, we are not really justified in interpreting a particular autoxidation reaction in terms of the mechanism of another unless the two reactions exhibit substantial similarities.

PREVIOUSLY REPORTED OBSERVATIONS OF ALKALI CELLULOSE AUTOXIDATION

A vast amount of research has been carried out on the alkali cellulose autoxidation reaction. Any mechanism must be in agreement with the facts of the reaction in order to be tenable; so it will be useful to make a concise list of these for reference.

1. Alkali cellulose autoxidation proceeds only under strongly alkaline conditions.

Only above 1M sodium hydroxide concentration does alkali cellulose autoxidize appreciably. It has been well substantiated that a peak in reaction rate (oxygen uptake) occurs at 6 to 8M sodium hydroxide concentration, as measured in the steeping liquor (4, 7, 8, 16). If alkali cellulose is completely dried, it is stable to oxygen (9).

2. Autoxidation occurs only in pressed alkali cellulose. Cellulose is stable at low consistencies in strong alkali solution.

A thorough study of the effect of cellulose consistency on autoxidation rate has not been reported. It is well established, however, that if cellulose is left in a slurry at 5% consistency, autoxidation does not occur (17, 18). The usual explanation for the lack of autoxidation in unpressed alkali cellulose has been that oxygen could not get to the cellulose unless it is pressed. Normal aging does occur when pressed alkali cellulose is immersed in ether (6), so this explanation is not entirely acceptable. Entwistle and co-workers (7) found that a 20% increase in the amount of alkali solution present in pressed alkali cellulose did not appreciably alter the rate of oxygen consumption.

3. Oxygen consumption is a phenomenon interrelated with depolymerization.

If oxygen is carefully excluded from alkali cellulose, its molecular weight will not decrease very much with time. Waentig (19) found that less degradation occurred if alkali cellulose was placed in a vacuum. Kita and Sakurada (20) found that if alkali cellulose is aged in hydrogen gas, it does not suffer as great a loss in viscosity as when aged in air. A nitrogen atmosphere also retards aging (21). Mitchell (22) found that the reaction occurring in the absence of oxygen is very slow and reduces the residual cellulose to yellowish-brown water-soluble products.

4. The initial oxygen consumption rate is proportional to the copper-number reducing value of the regenerated cellulose.

This was a finding of Entwistle and co-workers (7). The correlation suggests that the processes are similar in mechanism. A corollary to this observation is

the fact that when a sample of cellulose is used which has a very low copper number, an induction period is observed (7).

5. Oxygen is consumed at a constant rate after about 24 hours of aging.

Entwistle and co-workers (7) showed that the oxygen consumption rate for a wide variety of cellulose samples is constant after the initial differences, mentioned in Observation 4, have leveled out. This is a strong indication that the autoxidation reaction is a chain reaction.

6. Oxygen pressure is not rate-controlling in the range of conditions usually encountered.

Entwistle and co-workers (7) found that above 50 mm. of mercury the pressure of oxygen has only a minor effect on the rate of oxygen absorption of alkali cellulose. Below this pressure, the rate does start to fall sharply, however. When the alkali strength is 5.5M or 15M, the rate of oxygen consumption is lower than at 10M, but the consumption response to different oxygen pressures is almost identical at 5.5M to that at 15M. Since the solubility of oxygen is less at 15M than at 5.5M, we would expect a greater response of reaction rate with pressure at the higher molarity if the rate of oxygen diffusion was of any significance. The decrease in reaction rate beyond the peak at 6 to 8M sodium hydroxide concentration cannot be attributed, as was done by Davidson (4), to a decrease in the solubility of oxygen in the liquid phase.

7. Transition elements act as catalysts to alkali cellulose autoxidation.

A vast amount of work has been done on studies of transition element catalysts because of the technological importance to the viscose industry (4, 10, 23-26). Certain elements are positive catalysts, others are negative.

8. Both positive and negative catalysts lower the peroxide content of the alkali cellulose (26).

9. Many of the organic antioxidants which inhibit free radical autoxidations slow down the rate of alkali cellulose autoxidation.

Sodium thiocarbonate added to alkali cellulose in 0.08% concentration effectively prevents autoxidation (33). A number of typical antioxidants (26, 27) slow down autoxidation slightly, but do not cause total inhibition. A few have no effect at all.

10. Positive catalysts increase the amount of depolymerization that occurs for a given amount of oxygen consumed; negative catalysts decrease the amount of depolymerization for a given amount of oxygen consumed (26). In other words, catalysts have a more marked effect on depolymerization than on oxygen consumption.

11. Hydrogen peroxide is always present during autoxidation.

Entwistle and co-workers (26) found that hydrogen peroxide concentration increases during the initial phase of alkali cellulose autoxidation, and reaches a constant value of about 130 parts per million (based on alkali cellulose) when the reaction is at its steady-state condition.

12. About one carboxyl group is formed in aged alkali cellulose per cellulose chain (22, 28, 29).

13. The carbonyl content does not vary appreciably with aging time (28).

14. Considerable amounts of carbon dioxide are produced by the autoxidation reaction (16, 30, 31).

Estimates of carbon dioxide production range from 30 to 67% of the absorbed oxygen (molar basis).

15. The degradation that accompanies alkali cellulose autoxidation is a very random process.

This has been shown by many studies of the molecular weight distribution of alkali cellulose (21, 72, 80-89).

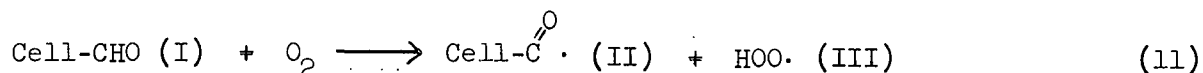
This brief list should aid us in analyzing the ramifications of various mechanisms in terms of what is known about the alkali cellulose autoxidation reaction. If a mechanism could explain all of the facts in this list, it would be at least partly verified.

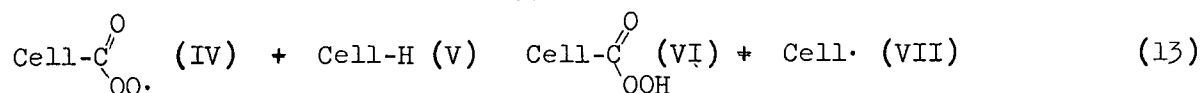
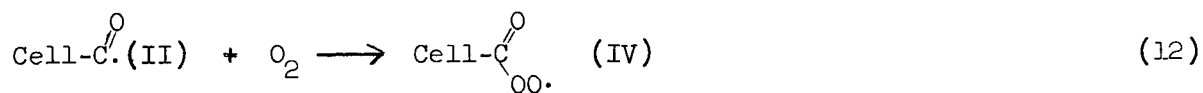
THE ENTWISTLE, COLE, AND WOODING
FREE RADICAL MECHANISM

In 1949, Entwistle, Cole, and Wooding (7, 26) proposed that the autoxidation of alkali cellulose proceeds by means of a sequence of free-radical reactions. They based their hypothesis upon analogy to olefinic hydrocarbon autoxidation, known to be of a free-radical nature. An extensive series of experiments was conducted on alkali cellulose in order to lend verification to the mechanism (7, 26). McBurney (34) reviewed the work of Entwistle and co-workers, and presented Equations (18) through (21) as a logical extension of the mechanism.

INITIATION

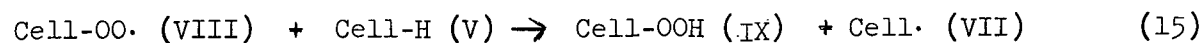
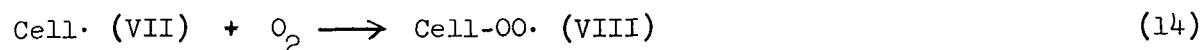
The initiation reaction is based on the correlation previously mentioned between copper number and initial autoxidation rate.





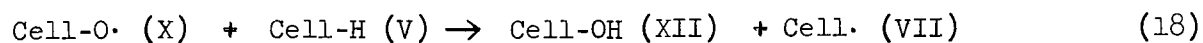
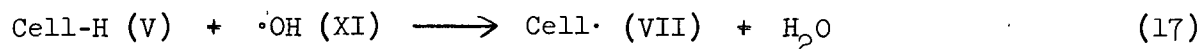
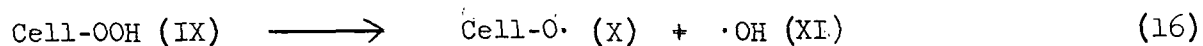
PROPAGATION

This sequence is repetitive until some termination occurs.

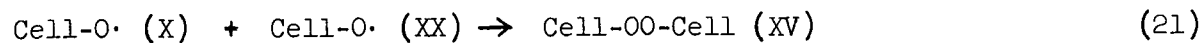
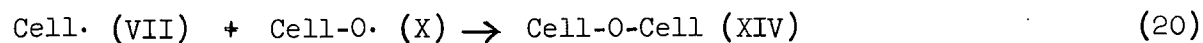
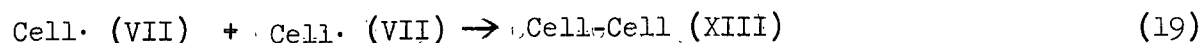


AUTOCATALYSIS

This is necessary to account for the autocatalytic behavior of the reaction.



POSSIBLE TERMINATION REACTIONS



Also:

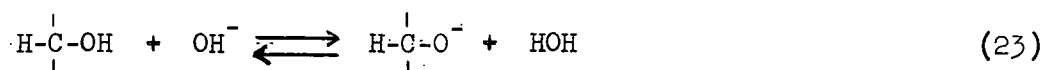


First, we should consider the evidence for this sequence of reactions.

Entwistle, Cole and Wooding based the initiation reaction on the correlation that they observed between copper number and oxygen consumption rate for freshly prepared alkali cellulose (Observation 4 of the previous section). The induction period, or period of initial inactivity, occurring when a cellulose sample is used that has a very low copper number, was believed to be important because such behavior is characteristic of olefinic hydrocarbon autoxidation. The constant rate period (Observation 5) was interpreted as evidence in favor of autocatalysis.

The effects of catalysts (Observation 7 to 10) were interpreted in a broad way as being indicative of a free radical mechanism. Hydrogen peroxide formation (Observation 11) was believed to be due to hydroperoxide hydrolysis and to free hydroxyl radical combinations.

The need for alkaline conditions (Observation 1) was explained through reference to the acidic nature of cellulose, at the hydroxyl hydrogen atoms. In strong alkali, cellulose anions would be formed.



This ionization would increase the electron density on the carbon atom, "activating" the hydrogen atom to an autoxidizable state.

It would seem, then, that this mechanism is a broad and adequate theory for explaining the autoxidation of alkali cellulose. It is consistent with certain facts of the reaction, and is presented in terms of a conventional mechanism. Certain inconsistencies and shortcomings must be considered, however.

First of all, no direct evidence for the existence of free radicals in autoxidizing alkali cellulose has ever been obtained. The catalysis studies of Entwistle

and co-workers (26) appear to be the strongest evidence yet presented. They found that when benzenediazonium hydroxide is added, the reaction rate increases. Benzenediazonium hydroxide behaves as an acid in alkali, being converted to a diazotate salt. They claim that this decomposes in strong alkali (5.5M in Entwistle and co-workers' experiment) to free phenyl radical, nitrogen, and free hydroxyl radical. The production of the latter was thought to be responsible for the increase in reaction rate and the experiment was taken as evidence for the free radical mechanism. However, they stated that at the time the alkali cellulose was placed in the apparatus for determining the rate of oxygen absorption, no nitrogen was being evolved. After this delay, free hydroxyl concentration would by necessity be zero, for it is a very fugitive radical, especially in a system containing aromatic compounds (35).

Perhaps the most difficult aspect of the free radical mechanism to accept concerns the hydroperoxide intermediate. Walling has discussed in detail how important it is that the hydroperoxide be stable; otherwise it is not available for autocatalytic purposes (12). Since any cellulose hydroperoxide would be readily hydrolyzed to hydrogen peroxide (5, 32) by strong alkali, it cannot be considered stable; hence, it is difficult to see how the autocatalysis step can operate. The dissociation energy of hydrogen peroxide at the oxygen-to-oxygen bond is about 53 kg.-cal./mole, as opposed to 33 kg.-cal./mole in the hydroperoxide (36, 37). The hydroperoxide is therefore a much more active radical source for autocatalysis.

Kinetics is another important consideration. In this respect, alkali cellulose autoxidation is distinctly different from olefinic hydrocarbon autoxidation. Entwistle, Cole, and Wooding discovered that the initial rate of oxygen consumption is proportional to the copper number of the cellulose. They assumed that the

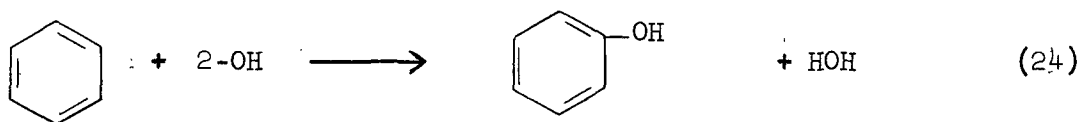
copper number was synonymous with aldehyde content. Now, if in alkali cellulose autoxidation, the initial rate of oxygen absorption is proportional to the aldehyde content, we are dealing with a wholly different kind of reaction than olefinic hydrocarbon or aldehyde autoxidation of the kind previously discussed, for in such reactions the initial rate of oxygen consumption is essentially zero. These hydrocarbon or aldehyde autoxidations increase speed very slowly at first, and at a rate proportional to the hydroperoxide content. The very high initial oxygen consumption rate that is observed in alkali cellulose, prepared freshly from cellulose of high copper number, cannot be explained by analogy to these hydrocarbon autoxidations.

There are many other points where the free radical mechanism is not satisfactory. There is no suggestion from this mechanism as to why pressing is necessary (Observation 2), why both positive and negative catalysts lower hydrogen peroxide content (Observation 8), why catalysts affect the ratio of oxygen absorbed to degradation (Observation 10), why carboxyl and carbonyl contents behave as they do (Observations 12 and 13), why so much carbon dioxide is formed (Observation 14), or why degradation is so uniform (Observation 15). What is most important, however, is the realization that: (1) no direct evidence has ever been obtained in this system for the presence of free radicals, and (2) the basis for the free radical mechanism, as it now stands, is not sufficient to prove that it is a valid mechanism.

METHODS

DETECTION OF THE FREE HYDROXYL RADICAL

The free hydroxyl radical undergoes a number of reactions that have been extensively studied. This free radical reacts very vigorously with benzene and benzene derivatives in aqueous solution, resulting in hydroxylation of the aromatic nucleus:



This reaction has been given a large amount of attention in recent years, although the conversion of benzene to phenol was known as early as 1900 (39). When benzene is used as the substrate, phenol and biphenyl are the major products, provided that the benzene is present in great excess (40, 42-46). If benzene is treated with excess free hydroxyl radical, a complex polyphenolic mixture is obtained. Reaction 24 is a very fast reaction (35), and goes by way of an intermediate that is an addition product of the free hydroxyl radical and the aromatic compound.

The reaction apparently occurs with any aromatic substance. Nitrobenzene (48), benzoic acid (40, 43-45, 49) and 1-naphthalenesulfonic acid (50) yield mixtures of hydroxylated isomers.

It has been shown (51, 52) that the free hydroxyl radical produced by the Fenton reagent, which is a mixture of a ferrous salt and hydrogen peroxide in dilute acid, is responsible for the aromatic hydroxylation reaction. Stein and Weiss (44) have shown that there is only a slight pH dependence in the production of phenol from a solution of benzene in water, using x-rays to produce the free

hydroxyl radicals. A shallow minimum in phenol production occurs at pH 7, the curve rising slightly at pH 2 and at pH 14.

APPLICATION OF THE REACTION OF FREE HYDROXYL RADICALS WITH AROMATIC SUBSTANCES TO THE AUTOXIDATION OF ALKALI CELLULOSE

The free radical mechanism predicts that the free hydroxyl radical is an important intermediate at the autocatalysis step of alkali cellulose autoxidation. If the free radical mechanism is true, the presence of benzene during the aging of alkali cellulose should result in the formation of phenol. Likewise, benzoic acid, 1-naphthalenesulfonic acid and other aromatics should all be able to inhibit the autoxidation. Inhibition of oxygen consumption and of molecular weight loss should be observed.

Entwistle, Cole, and Wooding did not indicate how much free hydroxyl radical formation could be expected during alkali cellulose autoxidation. Fortunately, it has been possible to make an estimate of the amount of free hydroxyl radical formation from theoretical considerations, and, from this, of the amount of phenol that would be formed from the reaction of benzene with autoxidizing alkali cellulose. The reaction of benzene with free hydroxyl radicals has been reported only up to a pH value of 14, which would correspond to a molarity of roughly 1 (44). It was necessary, therefore, to measure phenol yields from the free hydroxyl radical reaction with benzene at 5M sodium hydroxide, where the autoxidation reaction operates. Free hydroxyl radicals were generated for control purposes by the action of x-rays on 5M aqueous sodium hydroxide for the homolysis of water is independent of pH.

Three systems were investigated by the x-ray technique. First, benzene-saturated water was irradiated in order to compare the analytical techniques and

x-ray dosages with those used by Stein and Weiss (44). Second, benzene-saturated 5M sodium hydroxide was irradiated. This made it possible to calculate phenol yields based on a known amount of free hydroxyl radical, and also to demonstrate directly that phenol will form in 5M sodium hydroxide from the reaction of benzene with free hydroxyl radical. The third system that was studied in the x-ray work was alkali cellulose containing benzene. The irradiated samples were analyzed for phenol in order to demonstrate that phenol was produced from benzene and free hydroxyl radicals in the presence of alkali cellulose.

In an auxiliary experiment, the concentration of benzene in a saturated solution of benzene in 5M sodium hydroxide was determined. This served as an aid in comparing the phenol yields obtained by Stein and Weiss to those obtained in this work.

Phenol Production Study

A study was then conducted on the effect of the autoxidation of alkali cellulose on benzene. A large batch of alkali cellulose was prepared, and divided into two portions. Benzene was added to one portion, and the other was used as a control. After aging, both samples were analyzed for their phenol content. Auxiliary experiments were conducted in order to demonstrate that phenol is stable in autoxidizing alkali cellulose.

Inhibition Studies

The rate of oxygen consumption of a control sample of alkali cellulose was determined at a given temperature and oxygen pressure. This was compared with the rates of oxygen consumption of samples containing (1) benzoic acid and (2) 1-naphthalenesulfonic acid.

A further check of the inhibitory effects of free hydroxyl radical couplers was conducted by following the depolymerization of alkali cellulose samples with time. In this experiment it was possible to assess the inhibitory effects of (1) benzoic acid, (2) 1-naphthalenesulfonic acid and (3) benzene.

PHENOL AS AN INHIBITOR

It has already been mentioned that it was necessary to conduct an autoxidation containing a known amount of phenol, in order to determine its stability in autoxidizing alkali cellulose. This afforded a good opportunity to determine the inhibitory effect of phenol on alkali cellulose. Samples of cellulose were regenerated for intrinsic viscosity determination at initial and final times. The comparison of viscosities showed whether or not inhibition had occurred.

Phenol is a typical antioxidant in conventional free radical autoxidations (62), so this experiment yielded evidence as to whether or not alkali cellulose autoxidation is a free radical reaction.

PHOTOCATALYSIS STUDY

One of the most basic methods of investigating a free radical reaction is to observe the effect of light on the reaction (53). Reactions such as the ones proposed by Entwistle, Cole, and Wooding should invariably be photocatalytic, for the rate-controlling step is a spontaneous dissociation of a hydroperoxide into a free radical pair, a process that can be stimulated by light photons.

In order to determine whether or not alkali cellulose autoxidation is photocatalytic, it was necessary to age one sample in the dark, and an identical sample under illumination, and compare their subsequent depolymerization. Accordingly, two cells were constructed for aging alkali cellulose; one was clear pyrex glass;

the other was a similar cell, but enameled black. Alkali cellulose was placed in these; aging was allowed, and intrinsic viscosities were determined on the regenerated cellulose samples.

In this work, visible light has been used. Trautz and Thomas have shown that visible light (90) has a profound effect on the rate of oxygen consumption of various autoxidizable substances. Benzaldehyde autoxidation was accelerated by a factor of 17 by the action of violet light, alkaline pyrogallol autoxidation by a factor of 8 by the action of red light. In certain cases, there was an inhibitory effect by the action of light. Ultraviolet light could not be used in this experiment, for it would have introduced degradation of the cellulose molecules whether or not it influenced the autoxidation reaction.

ELECTRON PARAMAGNETIC RESONANCE METHODS

A recent development in free radical chemistry has been the detection and analysis of microwave spectra resulting from the resonance of unpaired electrons. Detailed accounts of the method, and progress in its application, appear in the Annual Reviews of Physical Chemistry, from 1955 to date (54). Essentially, electron paramagnetic resonance (EPR) is spectroscopy extended into the microwave region, where unpaired electrons resonate. If the electron is in the vicinity of a nucleus with a net magnetic moment, it will give an absorption band in the EPR spectrum. The method is sensitive to a remarkably low level; resonances have been obtained from biological materials of the range of 10^{-6} to 10^{-8} moles of unpaired spins per gram (55).

Studies have generally been restricted to simple, well-defined systems. An instance may be cited (56) in which a more complex system has been successfully investigated; Bamford and co-workers have studied the kinetics of a free radical

polymerization by EPR. Also, Ott (57) obtained evidence of the existence of two types of free radicals from ball-milled cellulose.

PROCEDURES

GENERAL PROCEDURES

CELLULOSE

Acetate-grade cotton linters (Buckeye Cellulose Corporation) were used throughout this work.

CHEMICALS

Reagent-grade chemicals were used except where specified otherwise.

WATER

Two types of purified water were used. In general, ordinary distilled water was used throughout. In certain experiments, this was redistilled from alkaline permanganate solution. Such water will be referred to as redistilled water. Its use was required in the phenol determinations, as ordinary distilled water gave a color in this test.

ALKALI CELLULOSE

The cellulose was mixed with 5M sodium hydroxide solution, at consistencies ranging from 5 to 15%. After steeping at room temperature for one hour some of the excess alkali solution was removed by vacuum filtration with the aid of a rubber dam on the semidry pad. The alkali cellulose was then transferred to a stainless steel box for pressing. Pressing was done on a Carver hand press with 6-inch square platens, until the desired consistency of approximately 28% was reached.

BENZENE

Reagent-grade (thiophene-free) benzene was extracted three times with approximately equal volumes of 5M sodium hydroxide solution to remove traces of phenol.

REGENERATION OF ALKALI CELLULOSE FOR VISCOSITY DETERMINATION

A sample of alkali cellulose (3 to 10 grams) was placed in a Waring Blendor with 150 ml. of 5% acetic acid. The blendor was run at moderate to slow speed, just long enough to disperse any lumps. The slurry was filtered through a sintered glass funnel (medium), washed with distilled water until neutral, then washed with about 50 ml. of acetone, and allowed to air dry.

This neutralization reprecipitated the alkali-soluble fraction of the cellulose, avoiding falsely high viscosity readings. As the cellulose had been dried with acetone, it was easily dispersed in the cupriethylenediamine.

DETECTION OF THE FREE HYDROXYL RADICAL

CONTROL STUDIES USING X-RAY

In this study, free hydroxyl radicals were generated by the action of x-rays on water, in order to demonstrate that the free hydroxyl reacts with benzene in the alkali cellulose system.

Equipment

The x-ray equipment used in this work was at St. Elizabeth Hospital in Appleton, Wisconsin. The unit produced an estimated 800 roentgen per minute dose of 280 kv. x-rays at the exit window, and employed a tungsten target.

The reaction cell was a cylindrical crystallizing dish, 70 mm. in diameter, and 50 mm. in height. In some of the earlier work, the reaction cell was covered with a sheet of plastic film, but in later work this was replaced by a glass plate, ground to a close fit.

X-Ray Study on Water Saturated with Benzene (Experiment 1)

This run was conducted in order to test the methods being used, and also to compare the results with those of Stein and Weiss (44).

A saturated solution of benzene in water was prepared, using alkali-extracted benzene and redistilled water. Two samples of 100 ml. each were drawn off, and stored in 125-ml. Erlenmeyer flasks, with glass stoppers. An excess of 0.25 gram of benzene was added to each to assure that saturation would persist during handling.

One of the samples was poured into the irradiation cell. It was covered with a glass plate and irradiated for 5 minutes. The sample was returned to the bottle and brought back to the laboratory for phenol analysis.

Both samples were acidified to pH 3.0 with 8.5% phosphoric acid and extracted 5 times with 20-ml. portions of diethyl ether. The ether extracts were combined and extracted 3 times with 5-ml. portions of 0.1M sodium hydroxide solution. The combined alkaline extracts were warmed to expel dissolved ether, neutralized to pH 7.0 and diluted to 25 ml. for phenol analysis (Appendix IV).

X-Ray Studies on 5M Sodium Hydroxide Solution Saturated With Benzene (Experiments 3, 4, and 5)

Saturated solutions of benzene in 5M sodium hydroxide were prepared by shaking 100 ml. each of benzene and 5M sodium hydroxide in a separatory funnel. After the solution had clarified, the alkali layer was drawn off for use.

Each experiment consisted of an irradiated sample and a nonirradiated control sample. After irradiation as described in the general instructions, the samples were neutralized with concentrated hydrochloric acid. The neutralized samples were extracted and analyzed for phenol in exactly the same manner as in the run with benzene-saturated water (p. 24).

The special conditions at which each run was conducted are given in Table II, p. 37.

X-Ray Studies on Alkali Cellulose Containing Benzene
(Experiment 5)

This experiment was simply to show that the reaction of free hydroxyl radicals with benzene would occur if the free hydroxyls were generated in alkali cellulose, with benzene as an added substrate. Earlier attempts were frustrated by several experimental difficulties. One difficulty arose from the loss of benzene from the alkali cellulose during the pressing and subsequent handling, as benzene is quite volatile. This was overcome by adding the benzene after alkali cellulose preparation. High and variable blanks were obtained on the phenol analysis from unirradiated samples. It was discovered that the compound causing the blank was a by-product of the autoxidation reaction. This problem was solved by a distillation procedure which separated the interfering substance. Extraction procedures that worked for phenol in trial solutions did not work when they were applied to alkali cellulose extracts, and required modification. The final run is being reported here.

Cellulose purified by boiling in 5% sodium hydroxide, as described in Appendix II, Method B, was used. Alkali cellulose was prepared from this in the normal way. The pressed alkali cellulose was placed in a polyethylene bag, along

with 2 ml. of benzene, and kneaded until the lumps were dispersed. Equal portions were packed into two tared reaction cells, each containing 1 ml. of benzene. The cells were covered with glass plates and allowed to stand for about 4 hours before irradiation, in order for the benzene to diffuse through the alkali cellulose. One of the samples was then irradiated for 10 minutes.

The alkali cellulose samples were transferred to sintered glass funnels for washing. During this transfer the odor of benzene was present, which shows that there was benzene in the samples during irradiation. The samples were washed with 50 ml. of redistilled water in small increments, then with 100 ml. of dilute hydrochloric acid (20 ml. of concentrated hydrochloric acid diluted to 100 ml. with redistilled water), and finally with redistilled water until 400 ml. of washings were collected.

The washings of each were neutralized with concentrated hydrochloric acid, and adjusted to pH 3.0 with 8.5% phosphoric acid. One hundred grams of sodium chloride were added to each of the acidified extracts, and they were extracted 4 times with 50-ml. portions of chloroform. The combined chloroform extracts of each of the samples were extracted 3 times with 20-ml. portions of 0.1M sodium hydroxide solution.

Both of the combined 0.1M alkaline extracts were neutralized to pH 8.0 with dilute hydrochloric acid and treated with 10 ml. of pH 8.0 buffer solution (8% $\text{Na}_2\text{HPO}_4 \cdot \text{H}_2\text{O}$ adjusted to pH 8.0 with 5M sodium hydroxide). Each sample was treated with 8 g. of sodium chloride and then distilled, 50 ml. of distillate being collected in each case. The distillates were analyzed for phenol by the diazo method (Appendix IV).

DETECTION OF PHENOL IN AUTOXIDIZING ALKALI CELLULOSE WHICH
CONTAINED BENZENE (EXPERIMENTS 6 and 7)

The cellulose was purified in three stages (Appendix II, Method A) which included a chlorite cook, a dilute alkali cook, and a 5M alkali steep.

About 200 grams of this cellulose was then converted into alkali cellulose with 5M sodium hydroxide solution as previously described. After being thoroughly homogenized by kneading in a polyethylene bag, the alkali cellulose was divided into two equal portions; half was placed in a one liter Erlenmeyer flask as a control; the other half was placed in a similar flask which contained 5 ml. of alkali-extracted benzene. The alkali cellulose nearly filled the flasks.

In order to guard against a total loss of benzene during the autoxidation period, a 15 by 150 mm. test tube was pushed down into the alkali cellulose in the sample which contained benzene, and filled with alkali-extracted benzene, as illustrated in Fig. 1. This provided an atmosphere saturated with benzene at the mouth of the flask.

The two samples were partly closed with small Erlenmeyer flasks, and placed in a 30°C. constant-temperature bath for 10 days.

At the end of this aging period, the alkali cellulose was removed from the flasks and analyzed for phenol. The alkali cellulose of Experiment 7 was analyzed for benzene after aging, but it was not in Experiment 6, as described in Appendix V.

The aged alkali cellulose was extracted for phenol as described in Appendix III. Briefly, the aged alkali cellulose samples were transferred to sintered glass funnels for washing. The samples were washed with 100 ml. of redistilled water in small increments, then with 300 ml. of dilute hydrochloric acid (100 ml.

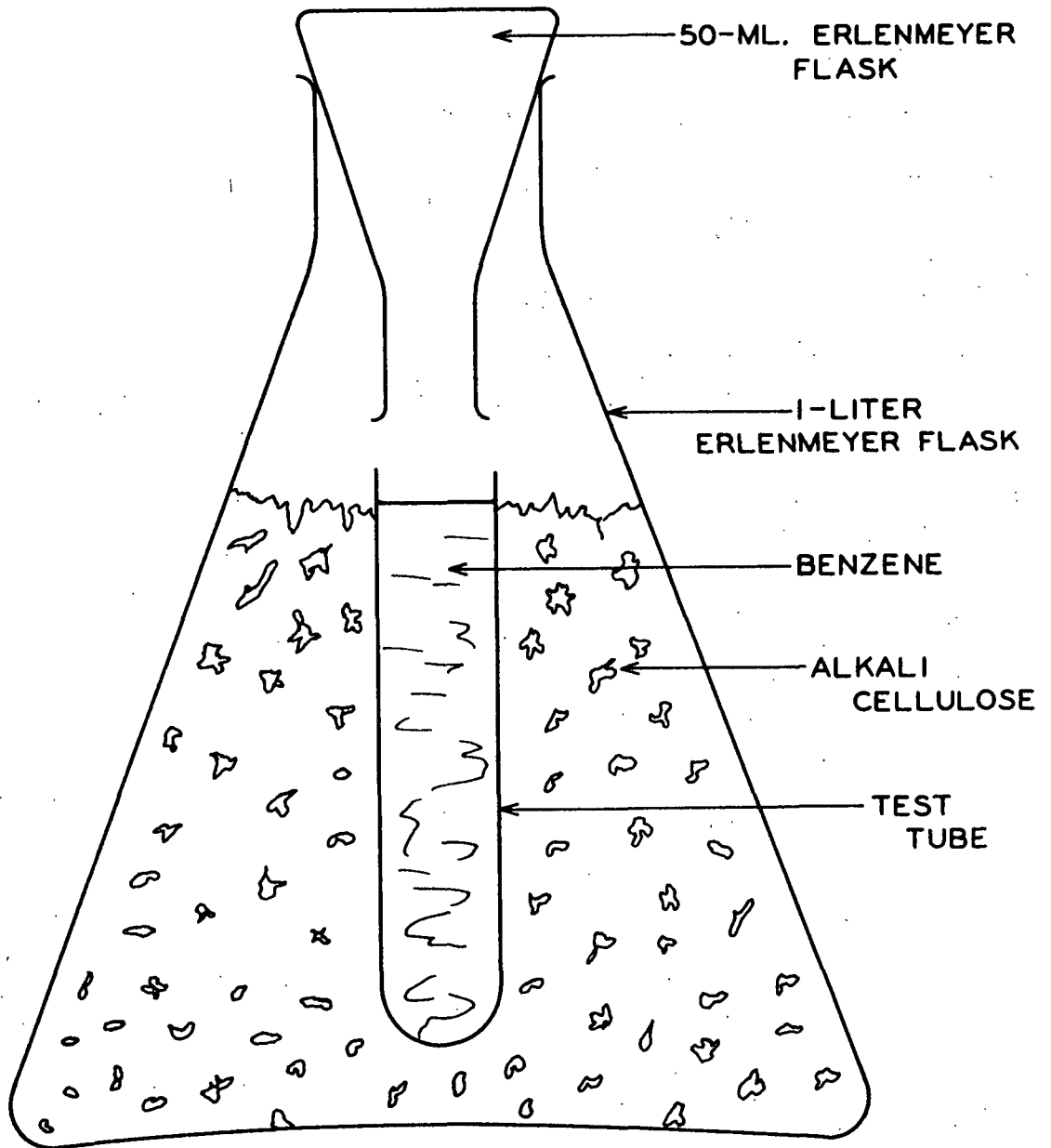


Figure 1. Apparatus for Aging Cellulose in the Presence of Benzene

of concentrated hydrochloric acid diluted to 300 ml. with redistilled water), and finally with redistilled water until 1000 ml. of washings were collected. The 1000 ml. of washings were acidified to pH 3.0, and 200 g. of sodium chloride were added. It was then extracted with chloroform. The chloroform extract was extracted with dilute sodium hydroxide. The alkaline extract was treated with sodium chloride and buffer, the pH adjusted to 8.0 and distillation employed. This distillate (100 ml.) was analyzed for phenol (Appendix IV).

INHIBITION STUDIES, USING FREE HYDROXYL RADICAL COUPLERS

Oxygen Absorption Measurements (Experiment 8)

It was necessary to use nonvolatile aromatic substances in this work, because of the nature of the gas-measuring device. Benzoic acid and 1-naphthalenesulfonic acid were used as coupling agents, as they react with free hydroxyl in the same way as does benzene (40, 43-45, 49, 50).

Benzoic acid, Mallinckrodt Analytical Reagent grade, was used. The 1-naphthalenesulfonic acid dihydrate was synthesized (58) and recrystallized from 20% hydrochloric acid, m.p. 89.5°C. (reported, 90°C.) (58). These substances were added directly to the steeping liquor.

The oxygen absorption rate was determined by the method described by Entwistle, Cole, and Wooding (7). This method is particularly useful because of its high sensitivity, and also because the rate of oxygen consumption, not the total consumption, is determined.

Four runs were made which were of interest; two were with plain alkali cellulose, one with benzoic acid, and the other with 1-naphthalenesulfonic acid. A hypochlorite-oxidized cotton linter was used in order to have a cellulose with a

rapid initial oxygen consumption. The procedure used for this oxidation is given on p. 33. The cellulose used on the control runs and on the 1-naphthalenesulfonic acid run was treated with 250 ml. of hypochlorite solution and 200 ml. of buffer; the cellulose used on the benzoic acid run was treated with only 125 ml. of the hypochlorite solution and 100 ml. of the buffer.

Intrinsic Viscosity Change

The second method of observing inhibition of alkali cellulose autoxidation was to follow the rate of depolymerization in the presence of known aromatic inhibitors.

Two runs are reported; the first (Experiment 9) using benzoic acid, and 1-naphthalenesulfonic acid; the second (Experiment 10) was conducted using benzene.

Experiment 9

Six-hundred grams of cellulose were purified by the organic solvent extraction method described in Appendix II, Method C. From this cellulose, 3 batches of alkali cellulose were prepared: (a) the control, (b) alkali cellulose containing benzoic acid and (c) alkali cellulose containing 1-naphthalenesulfonic acid.

In preparing each of these samples, 110 g. of the purified cellulose were steeped in 800 ml. of 5M sodium hydroxide solution for 1 hour at room temperature (27°C.). The alkali cellulose samples were then pressed to approximately 29% consistency. The benzoic acid and 1-naphthalenesulfonic acid samples were prepared by adding 1.6 g. of the acids to the steeping liquors.

The alkali cellulose was packed loosely into one-liter Erlenmeyer flasks, and placed in a 30°C. water bath for aging. Samples of each flask were removed

daily and regenerated in 5% acetic acid (using a Waring Blendor) for intrinsic viscosity determinations in 0.5M cupriethylenediamine. The intrinsic viscosities were determined by extrapolating the reduced viscosity measurements to zero concentration.

Experiment 10

Samples of cellulose were regenerated from the "Benzene" and "Control" samples of Experiment 6 of the phenol detection studies, p. 27 to 29. The intrinsic viscosities were determined as described in Experiment 9.

PHENOL AS AN INHIBITOR

In this study, the effect of phenol on the depolymerization of alkali cellulose was determined. The cellulose samples were the same as those of the phenol stability study, the description and preparation of which is given on p. 92 to 93. The high-level run, containing 0.004% phenol, was the one sampled.

The intrinsic viscosities of regenerated cellulose samples were determined as described in Experiment 9.

PHOTOCATALYSIS STUDY

This was an experiment designed to show whether or not autoxidation of alkali cellulose is catalyzed by visible light, like many free radical reactions.

APPARATUS

Two pyrex Petri dishes, 150 by 20 mm., were used for reaction cells. One was made into a "dark" cell by painting the outer surface of both halves with black enamel. When it was assembled it made a light-tight box. A notch was cut

into the edge of each half of the dishes with a glass saw, large enough to permit the insertion of a thermometer (-10 to 110°C.) in the radial position, and still permit the dish to be fully closed to light.

A 15 w. fluorescent lamp with a General Electric "Daylight" illuminator was used as a light source. The fixture and lamp were placed in a 12 by 12 by 16.5 inch corrugated carton. The entire inner surface of the carton was lined with aluminum foil, in order to increase the intensity of the illumination. The Petri dishes were placed on a rack 2 inches high, so that they would be illuminated from both sides. The light intensity measured at the surface of the "light" cell was 13 foot-candles at the upper surface and 3.2 foot-candles at the lower surface, as determined by a Weston Master III light meter. The cells will henceforth be referred to as the "light" and "dark" cells.

EXPERIMENT

The cellulose that was used in this experiment had been purified according to the procedure of Appendix II, Method B. This involved a 5% alkali cook.

Alkali cellulose was prepared from a 35-g. sample of this cellulose in the usual manner. A sample of this alkali cellulose was regenerated to cellulose in 5% acetic acid at the beginning of the aging period. The remainder of the alkali cellulose (128 g.) was divided into two equal portions, which were placed in the two reaction cells. The temperatures of the two cells were recorded daily. At the end of 12,960 minutes, a sample from the "light" cell and one from the "dark" cell were regenerated in 5% acetic acid. Intrinsic viscosity determinations in 0.5M cupriethylenediamine were run on these two samples and the original regenerated cellulose to check for the presence of a photocatalytic effect.

ELECTRON PARAMAGNETIC RESONANCE STUDY

PREPARATION OF SAMPLES

A hypochlorite-oxidized cellulose was used for this study. It was prepared as follows. Chlorine gas was bubbled into normal sodium hydroxide solution until the pH dropped to 10.5. A 187.5-ml. portion of this, along with 150 ml. of normal potassium acid phosphate (monobasic) was diluted to 2000 ml., to which was added 160 grams of cotton linters. The suspension was kept at room temperature for 24 hours.

The sample was dewatered on a Buchner funnel under vacuum, pressing with a rubber dam. It was washed 4 times in 3-liter portions of distilled water, by slurring. After each washing, the sample was dewatered as above. Metal ions were removed (92) by boiling the entire sample for 20 minutes in 3 liters of water containing 0.042 g. of ethylenediaminetetraacetic acid, adjusted to a pH of 3.0. After this treatment the cellulose was washed as before. It was then air dried, and had a copper number of 3.1 by the method of Clibbens and Geake (74).

Alkali cellulose was prepared from about 2 g. of this and packed immediately into a pyrex sample tube of 3 mm. inner diameter to a depth of 1 inch. This was stored in a Dewar flask filled with crushed dry ice. The remainder of the sample was stored in a flask at 30°C. for aging. After 55 hours, it was again sampled, the sample being placed in a 3-mm. sample tube, as before. It also was stored in the Dewar flask at dry ice temperature. The EPR spectra were obtained 76 to 79 hours after the sample of alkali cellulose was first prepared.

OBTAINING THE EPR SPECTRA

The EPR spectra of these two samples were determined at the Institute for Enzyme Research at Madison, Wisconsin, on a Varian EPR spectrometer.

The Varian EPR spectrometer has a magnet with a pole diameter of 6 inches, and provides a field of 3300 gauss. During a run the field strength is varied by changing the current flow through the coils. The rate of sweep is also variable. The instrument achieves high sensitivity by modulating the 3-cm. wavelength signal at 100 kc. Both the amount of modulation and the power applied are variable. The cavity that the sample tube goes into is surrounded by a cooling jacket. Refrigeration of the cavity can be achieved with nitrogen passed through a coil immersed in liquid nitrogen.

For the samples of alkali cellulose taken to Madison, the full range of the instrument was employed in an attempt to locate free radicals. The two samples of the first run were run at $-150^{\circ}\text{C}.$, and no substantial free radical response was obtained.

In a single subsequent run, a sample of alkali cellulose was prepared in exactly the same way as in the first run, using the same cellulose. The EPR spectrum of the autoxidizing cellulose was determined at room temperature in a silica tube after 40 hours of aging.

DISCUSSION OF RESULTS

THE FREE HYDROXYL RADICAL

The presence of the free hydroxyl radical in autoxidizing alkali cellulose has been predicted by the free radical mechanism, and it is the objective of this experimental work to find out whether it can be detected.

The method used to detect free hydroxyl radicals had never been applied to alkali cellulose before, and so it was necessary to generate free radicals in alkali cellulose and in allied systems in order to prove its validity. It was also necessary to consider what the expected yield of free hydroxyl radical would be from alkali cellulose if the free radical mechanism is true.

FREE HYDROXYL RADICALS GENERATED BY X-RAY

The first experiment in this study was conducted on water saturated with benzene. The dosage had been estimated as being about 800 r./min. at the window of the unit, where the irradiation cell was placed. Since this same system had been studied by Stein and Weiss, comparison of phenol yields could be made, confirming the estimated radiation dosage. Work done by Johnson and Martin has shown the benzene-water system to be a reliable gamma-ray dosimeter (46); so a reasonably good check was expected. Table I shows the results.

The 0.25 g. excess of benzene was added to the water, saturated with benzene, in order to avoid evaporation losses during handling prior to irradiation. The excess benzene apparently caused no significant amount of phenol production due to its irradiation, for the yield obtained checked well with the work of Stein and Weiss (44). The blank was an identical sample which had not been irradiated. An earlier run, which lacked some of the refinements of this one, gave a value of 11

micrograms of phenol per 100 ml. of water, for each 1000 r. of exposure, which also agrees with the reported value (44).

TABLE I
X-RAY STUDY ON WATER, SATURATED WITH BENZENE
(Experiment 1)

Quantity of water, ml.	100
Amount of benzene	Saturated, + 0.25 g.
Cover on reaction cell	Glass plate
Duration of exposure, min.	5
Estimated dosage of x-rays, r.	4000
Energy of x-rays, kv.	280
Yield of phenol:	
Gross yield, $\mu\text{g.}$	38.6
Blank, $\mu\text{g.}$	<u>6.0</u>
Net yield, $\mu\text{g.}$	32.6
Yield of phenol, reduced basis	8 $\mu\text{g.}/100 \text{ ml. H}_2\text{O} \cdot 1000 \text{ r.}$
Yield, Stein and Weiss (<u>44</u>)	10 $\mu\text{g.}/100 \text{ ml. H}_2\text{O} \cdot 1000 \text{ r.}$

From this work we can conclude that the results of Stein and Weiss can be successfully duplicated with the arrangements and analyses used in this work. The radiation dosage, as calculated, was nearly correct at 800 r./minute of exposure.

Next, the irradiation of 5M sodium hydroxide solution which is saturated with benzene will be considered. The highest alkaline concentration employed by Stein and Weiss was 1M, and at this concentration they obtained higher yields of phenol than at neutrality. The results of three experiments at 5M are reported in Table II.

TABLE II

X-RAY STUDIES ON 5M SODIUM HYDROXIDE SOLUTION
SATURATED WITH BENZENE

	Experiment		
	2	3	4
Quantity of <u>5M</u> NaOH solution, ml.	100	100	100
Weight of water in solution, g.	98.8.	98.8.	98.8.
Cover on cell	Plastic film	Plastic film	Plastic film
Amount of benzene	Saturated	Saturated + 0.25 g.	Saturated + 0.25 g.
Duration of exposure, min.	5	5	5
Dosage of x-ray, r.	4000	4000	4000
Gross yield of phenol, $\mu\text{g.}$	11.0	27.0	20.6
Blank, $\mu\text{g.}$	3.8	2.5	7.0
Net yield of phenol, $\mu\text{g.}$	7.2	24.5	13.6
Yield, in $\mu\text{g./100 ml. H}_2\text{O}$ x 1000 r.	2	6	3

Although phenol was obtained in every instance, it was in considerably lower yield than when benzene-saturated water was the substrate (Table I).

The yield has been calculated on the basis of the water present, for this is the substance that is yielding the free hydroxyl radicals.

The solubility of benzene in 5M sodium hydroxide has been determined, and found to be 61 parts per million (Appendix V), or 0.0061%. The solubility of benzene in neutral water is approximately 0.15%, or approximately 25 times the solubility in 5M sodium hydroxide (44). On the basis of this reduced solubility

alone, the yield of phenol from a given amount of irradiation of the 5M sodium hydroxide-benzene system would be expected to be appreciably lower than in the water-benzene system. Stein and Weiss (44) studied the effect of benzene concentration on the phenol yield for a given amount of irradiation, and from this study it has been calculated that a yield reduction of about one-third would be experienced in the 5M sodium hydroxide-benzene system. This calculation was made on the basis of solubility differences. If this is applied to the phenol yield obtained on the water-benzene experiment reported in Table II, a yield of 5 μ g. phenol/100 ml. H_2O X 1000 r. is obtained, which is in agreement with the actual measurements in Table III.

It can be concluded, therefore, that the reaction of free hydroxyl radicals with benzene which occurs in benzene-saturated water also occurs in benzene-saturated 5M sodium hydroxide, but the yield of phenol is reduced. On the basis of the results obtained, the yield of phenol is reduced to about 40% of the yield in the water-benzene system.

The final investigation of the x-ray studies was the irradiation of alkali cellulose which contained benzene. The physical nature of alkali cellulose introduced difficulties. Because of its porous structure, the small amount of benzene that was dissolved in the liquid phase was easily lost by evaporation prior to irradiation. The first trials that were conducted failed to yield any phenol upon irradiation, presumably for this reason. Since the excess benzene that was added in the experiment with water caused no large increase in phenol, and the yields of phenol in the 5M sodium hydroxide work which contained the excess benzene were not larger than was expected, the assumption was made that excess benzene could be added to alkali cellulose, and the benzene not dissolved in the liquid phase would cause no appreciable phenol formation upon irradiation.

The excess benzene would insure that the liquid phase of the alkali cellulose would be saturated with benzene at the time of irradiation.

Another difficulty was the high apparent phenol content of the blank observed on nonirradiated alkali cellulose samples. This was apparently due to an autoxidation by-product, and was eliminated by a special distillation procedure (see Appendix III).

The results of irradiating alkali cellulose that contained benzene are given in Table III.

TABLE III
X-RAY STUDY ON ALKALI CELLULOSE WHICH
CONTAINED BENZENE
(Experiment 5)

Cellulose purification	See Appendix II, Method B
Weight of alkali cellulose, g.	112.4
Alkali strength	<u>5M</u> NaOH
Consistency	22.08% oven-dry cellulose
Amount of water, ml.	59.4
Duration of exposure, min.	10
Estimated dosage of x-rays, r.	8000
Yields of phenol	
Irradiated sample, μg .	48.0
Nonirradiated control, μg .	<u>00.0</u>
Net yield of phenol, μg .	48.0
Yield, in $\mu\text{g}/100 \text{ ml. H}_2\text{O} \cdot 1000 \text{ r}$.	10

The yield of phenol in this case was substantially higher than expected, when the yield is based on the amount of water present. Quite possibly additional free hydroxyl radicals were produced from the action of x-rays on the cellulose, which would react with benzene to form additional phenol. In any case, this experiment served to show that free hydroxyl radicals can be detected in the presence of alkali cellulose by adding benzene, and analyzing the phenol formed.

The control work on the free hydroxyl-benzene reaction with x-rays can be summarized as follows:

1. The production of phenol from water saturated with benzene by the action of x-rays has been confirmed. An entirely different analytical technique for phenol determination was used in this work than was used by Stein and Weiss (44).
2. Lower yields were obtained from irradiation of 5M sodium hydroxide saturated with benzene, than from water saturated with benzene. This was expected, for the solubility of benzene is greatly lowered by the salting-out effect of the sodium hydroxide.
3. If phenol yields are based solely upon the water present, irradiated 5M alkali cellulose containing benzene gives a greater yield of phenol than does the 5M alkali without the cellulose. This is evidence that some free hydroxyl radical comes from the cellulose during irradiation. When benzene was added to autoxidizing alkali cellulose in an attempt to detect free hydroxyl radicals that might be formed spontaneously (described in a future section of the discussion), very little phenol was detected; thus, the additional phenol could not have been formed by spontaneous hydroxyl radical formation.

4. When free hydroxyl radicals were generated in alkali cellulose which contains benzene, a high yield of phenol was obtained. This suggests that free hydroxyl radical reacted at a high rate with benzene, relative to alkali cellulose. It is known that the reaction of free hydroxyl radical with benzene is a very fast reaction (35). If free hydroxyl radicals are formed during alkali cellulose autoxidation, they would be able to react with an aromatic additive, forming a phenol.

It has therefore been established that the method selected to detect the free hydroxyl radical is valid in the alkali cellulose system. Next, an estimate will be made of the amount of phenol formation expected during autoxidation from considerations of the free radical mechanism.

ESTIMATE OF FREE HYDROXYL RADICAL AND PHENOL YIELDS

Assumptions

Certain assumptions must be made in order to arrive at any value for the phenol production. This estimate will be kept conservative; it will be the lowest phenol production that could be expected.

Oxygen Consumption Rate

The amount of autoxidation that has occurred in a given interval of time is based on the amount of oxygen absorbed by the alkali cellulose during that interval. Since the amount of oxygen cannot be conveniently measured in the autoxidation in the presence of benzene, an estimate was made from other data at the temperature of reaction (30°C.). The steady-state rate of oxygen consumption for autoxidizing alkali cellulose (5M NaOH, 30°C., 500 mm. of mercury oxygen pressure) has been

determined to be 7.5×10^{-4} ml. oxygen*, per g. cellulose x minute. This was determined with pure oxygen, at 500 mm. of mercury pressure. The autoxidations conducted for the purpose of measuring phenol production were conducted with air, which has about 175 mm. of mercury oxygen pressure. From the work of Entwistle, Cole and Wooding (7) it can be calculated that this change in oxygen pressure would reduce the rate of oxygen absorption to about two-thirds of the value of the higher pressure, or to 5.0×10^{-4} ml. oxygen, per g. cellulose x minute.

The only other consideration here is that nitrogen was present in the samples aged with air, and not in the samples which were used for oxygen consumption measurements. No evidence has been found in the literature that the presence of an inert gas makes any difference in the autoxidation rate. The nearly linear relationship between fluidity and time (Fig. 4) for alkali cellulose aging in air is a good indication that nitrogen did not accumulate in the reaction vessel to any appreciable degree and interfere with autoxidation.

The Yield of Phenol for a Given Amount of Free Hydroxyl Radical Production

Stein and Weiss (44) have reported that 0.75 mole of phenol is produced from 1 mole of free hydroxyl, reacting with benzene in the presence of oxygen. More recently, Johnson and Martin (46) have given the value as 1 mole of phenol per mole of free hydroxyl radical. Both of these values were obtained on water, saturated with benzene. The x-ray work done in this thesis suggests that the yield in 5M sodium hydroxide is only about 40% of that in water. If the more conservative estimate of yield of Stein and Weiss is taken, and this 40% correction

*The volume of oxygen is calculated at a temperature of 0°C. and at a pressure of 760 mm. of mercury.

is applied to it, a yield of 0.30 mole of phenol for each mole of free hydroxyl radical is obtained.

Estimate of Kinetic Chain Length

The amount of free hydroxyl radical that is produced will be inversely proportional to the kinetic chain length, so it is very important that an estimate of this be made. No theory exists for the prediction of kinetic chain length, and it is even sometimes difficult to determine. On well-defined reactions that are photocatalytic, the quantum yields may be determined, and it is usually assumed that the quantum yield is equal to the kinetic chain length. The quantum yield in the photo-oxidation of benzaldehyde has been determined to be between 10,000 and 15,000 (59); for the photo-oxidation of acetaldehyde, around 20 (60). With the use of more direct methods to determine kinetic chain lengths, styrene peroxide formation has a kinetic chain length of 10 to 40, depending on the catalyst used (61). The reaction of free hydroxyl radical with benzene is a chain reaction when oxygen is present (44); the kinetic chain length is 5.

Alkali cellulose is not comparable to systems that exhibit very long kinetic chains. In the first place, such systems must be free of impurities that could interrupt the chain process. Alkali cellulose is never as clean as freshly distilled benzaldehyde, for example. It always contains certain amounts of transition element impurities that would be capable of terminating a free radical kinetic chain. Systems with long kinetic chains are highly susceptible to inhibition and catalysis in general; alkali cellulose autoxidation is only moderately susceptible to catalysts, and is inhibited only in a moderate way. The fact that alkali cellulose autoxidation occurs in a sterically restricted system would also suggest that it could not reasonably be expected to possess long kinetic chains.

From this speculation it will be assumed that the kinetic chain length of the autoxidation of alkali cellulose is no more than 100 oxygen molecules per kinetic chain.

The relationship between kinetic chain length and hydroxyl radical production, it must be remembered, is a reciprocal one. The longer the chain, the less free hydroxyl, and the less phenol that could be produced if benzene were present. On the other hand, inhibition of the reaction is directly proportional to the kinetic chain length; so if the kinetic chain happened to be too long to permit measurable phenol production, the reaction would become extraordinarily sensitive to inhibition.

Calculation of the Expected Yield of Phenol

In a chain-propagated reaction proceeding by a free radical mechanism, as proposed by Entwistle, Cole and Wooding (7), a steady-state reaction rate is finally established. At this time, the rate of initiation is equal to the rate of termination. In order to know the total number of initiations or terminations that occur during a period of time, the total moles of reactant (oxygen) used during this period is divided by the kinetic chain length of the reaction. The kinetic chain length is the average number of repeated steps during the propagation sequence.

This relationship is expressed as follows. For a unit period of time, letting:

\underline{y} = the moles of substance that enter into an initiation reaction, such as



\underline{m} = the moles of total material used by the propagation reaction (oxygen)

\underline{c} = the kinetic chain length

then

$$\underline{y} = \frac{\underline{m}}{2\underline{c}} \quad (26)$$

The value of \underline{c} has been considered, and it was decided that it probably does not exceed 100. The value of \underline{m} has been determined (p. 42) to be 5.0×10^{-4} ml. oxygen/g. cellulose x minute, which would give a value of 0.0321 mole of oxygen for 100 grams of cellulose autoxidizing for 10 days. From Equation (26), a yield of 0.16 millimole of free hydroxyl is obtained for this amount of autoxidation.

Applying the yield factor of 0.30 for phenol production when benzene is present, a yield of phenol is obtained of 0.048 millimole (4.5 milligrams) for the autoxidation of 100 grams of cellulose for 10 days.

PHENOL PRODUCTION FROM BENZENE IN ALKALI CELLULOSE

Two long-term autoxidations were conducted in the presence of benzene. The amount of phenol detected is shown in Table IV.

The average net yield of phenol from these experiments was 8 micrograms of phenol per 100 g. of oven-dry cellulose per 10 days of aging. On an alkali cellulose basis, there was an average net yield of $2.5 \times 10^{-6}\%$ of phenol.

Experiments on the efficiency of the phenol recovery procedures used, described in Appendix III, showed that roughly 50% of an added amount of phenol was recoverable after aging for 10 days in the presence of alkali cellulose. Some of the loss was due to decomposition of the phenol; the rest of the loss was mechanical (see Appendix III, p. 90). These phenol recovery studies were on

TABLE IV

DETECTION OF PHENOL IN AUTOXIDIZING ALKALI CELLULOSE
WHICH CONTAINED BENZENE

	Over-all Data	
	Experiment	
	6	7
Cellulose purification	As in Appendix II, Method A	
Consistency of alkali cellulose, ovendry %	25.57	27.84
Alkali strength	5M NaOH	5M NaOH
Duration of aging, min.	14,130	12,960
Temperature of aging, °C.	30	30
Oxygen supply	Air	Air
Samples for Aging		
Sample with benzene		
Weight of alkali cellulose, g.	367	365
Amount of benzene		
Added initially, g.	4.4	4.4
Analyzed, after aging, g.	---	0.54
Weight of ovendry cellulose, g.	94	99
Control sample		
Weight of alkali cellulose, g.	368	364
Weight of ovendry cellulose, g.	94	96
Phenol determinations		
Sample with benzene, µg.	9	8
Control sample, µg.	1	2
Net phenol, reduced basis, µg.	9 ^a	7 ^a

^aPhenol per 100 g. cellulose x 10 days

phenol concentrations as low as $30 \times 10^{-6}\%$, which was ten times the amount found in the alkali cellulose aged in the presence of benzene. The losses seem to be proportional to the amount of phenol present, so the per cent loss should be about 50% regardless of the amount present.

It can be concluded, therefore, that no more than 16 micrograms of phenol per 100 g. oven-dry cellulose are produced from free hydroxyl reacting with benzene in alkali cellulose during ten days of aging. This is obtained by multiplying the average value from the two runs by a loss factor of two.

The predicted phenol yield was 4.5 milligrams per 100 g. oven-dry cellulose for ten days of aging. Thus, only 0.36% of the predicted yield was obtained.

The possibility that benzene did not diffuse to all parts of the alkali cellulose does not seem likely. Experiment 7 showed that there was at least 0.54 gram of benzene present at the end of the aging period (See Appendix V, p. 101 for analytical procedure for benzene in alkali cellulose). This amount was enough to saturate the atmosphere within the reaction vessel, and also to saturate the liquid phase of the alkali cellulose with benzene. According to Graham's law of diffusion, the rate of diffusion is inversely proportional to the square root of the molecular weight. The rate of diffusion of benzene would be about 58% that of oxygen on this basis. Since oxygen is capable of diffusing to all parts of the alkali cellulose without difficulty, no great difficulty can be expected from benzene. It should also be remembered that the solubility of benzene in 5M sodium hydroxide is 61 parts per million, and although the solubility of oxygen in 5M sodium hydroxide could not be found in the literature, it appears to be less

than 1 part per million.* Therefore, benzene should be able to diffuse into the alkali cellulose much more easily than oxygen.

Inhibition could also have caused a very low yield of phenol. If benzene were to react vigorously with the free hydroxyl radical intermediate, the autoxidation reaction would be effectively inhibited, and little additional free hydroxyl radical would be generated. But it will be seen in the next section of the discussion that no inhibition was observed from the action of benzene and other aromatic compounds on alkali cellulose autoxidation.

The experimental evidence that has been considered so far has shown that the free hydroxyl radical cannot be an important intermediate in alkali cellulose autoxidation.

INHIBITION STUDIES USING FREE HYDROXYL RADICAL COUPLERS

The inhibitory effects of benzene, benzoic acid, and 1-naphthalenesulfonic acid on autoxidizing alkali cellulose have been studied. Since these compounds have no easily oxidized or reduced functional groups, but react vigorously with the free hydroxyl radical, they should be very specific inhibitors for autoxidations in which the free hydroxyl radical is an important intermediate.

In Experiment 8, the effect of benzoic acid and 1-naphthalenesulfonic acid on the rate of oxygen consumption of alkali cellulose have been studied. The data for this experiment appear in Appendix I, and have been plotted in Fig. 2. Figure 2 shows the oxygen consumption rate of two control runs plotted on the

* Data of oxygen solubility in sodium hydroxide solutions up to 2M are given in International Critical Tables, III, p. 271. The three points that are listed give a straight-line relationship when plotted on semilog paper, and indicate that the solubility of oxygen in 5M sodium hydroxide is about 0.1 of the solubility in water. The solubility of oxygen in water at 30°C. and at atmospheric partial pressure is about 7 parts per million, so the solubility of oxygen in 5M sodium hydroxide would be expected to be about 0.7 part per million.

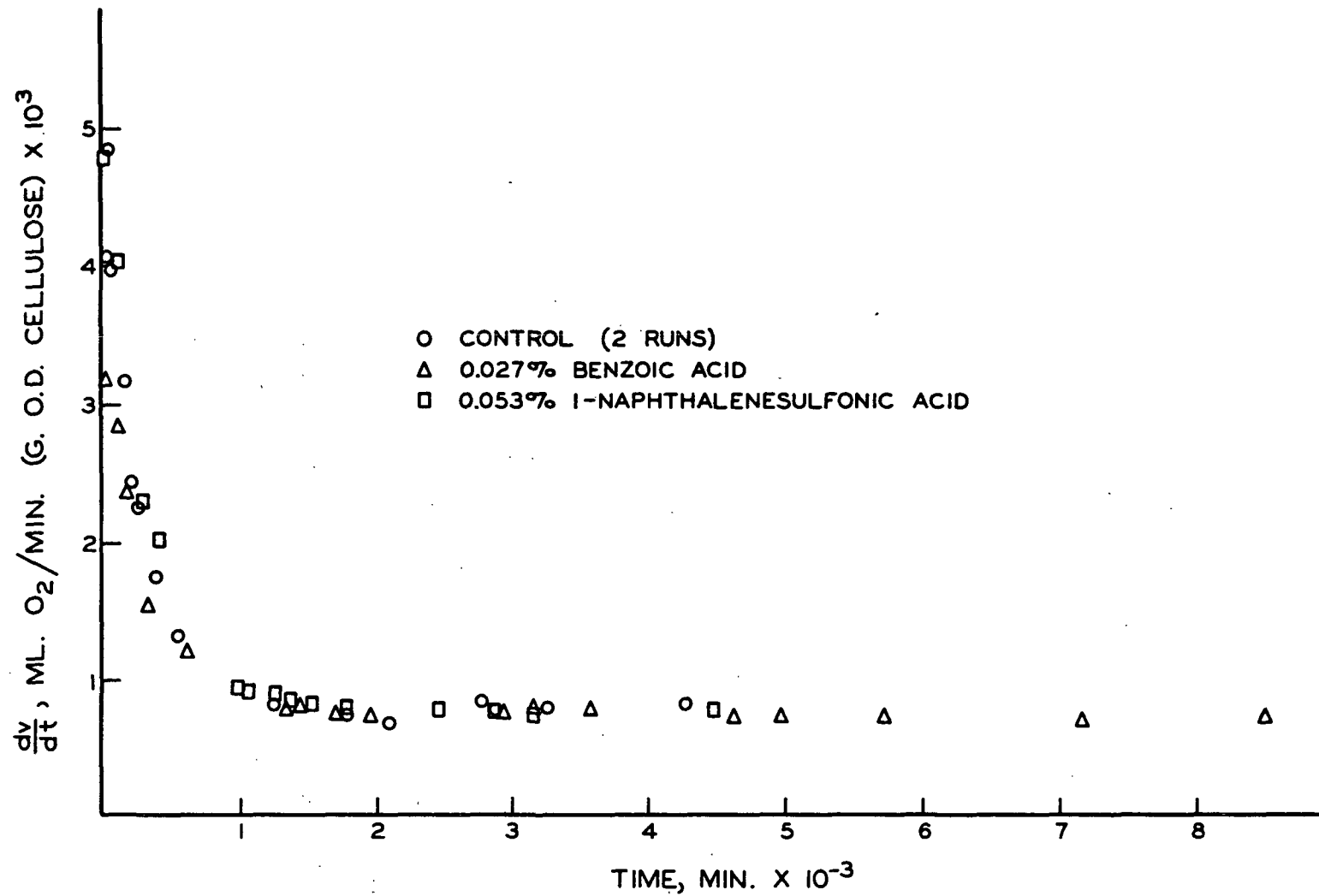


Figure 2. Effect of Free-Hydroxyl Couplers on the Oxygen Consumption Rate of Alkali Cellulose (Experiment 8).

same graph as the oxygen consumption rates of two alkali cellulose samples which contained these substances. The cellulose used on the benzoic acid run was of lower initial copper number than the cellulose of the other runs, and showed a lower initial rate of oxygen consumption. Otherwise, the rates of oxygen consumption were the same on all samples.

It therefore may be stated that substances which react with the free hydroxyl radical do not influence the rate of oxygen consumption of alkali cellulose. The conclusion is that the free hydroxyl radical is not involved with the reactions that incorporate oxygen into alkali cellulose.

The next series of experiments deal with the influence of free hydroxyl radical couplers on the depolymerization process that accompanies autoxidation. The data for these experiments (Experiments 9 and 10) are also listed in Appendix I, and have been plotted in Fig. 3, 4, and 5.

Figure 3 shows the change in intrinsic viscosity with time of a control sample of alkali cellulose, plus samples containing benzoic acid, and 1-naphthalene-sulfonic acid (Experiment 9). A common batch of purified cotton linters was used in preparing the alkali celluloses, and they were prepared as nearly alike as possible, but slight differences in pressing existed, which probably account for the tendency for the data to spread slightly with time. In general, it may be stated that all three batches degraded at the same rate.

If the rate of degradation is constant, and the attack is random on the cellulose molecule, a plot of intrinsic fluidity vs. time will give an approximate straight-line relationship. This kind of plot is shown for Experiment 9 in Fig. 4., and the line is, indeed, approximately straight. This demonstrates that when alkali cellulose is aged in air by the arrangement used in this work (Fig. 1, p. 28)

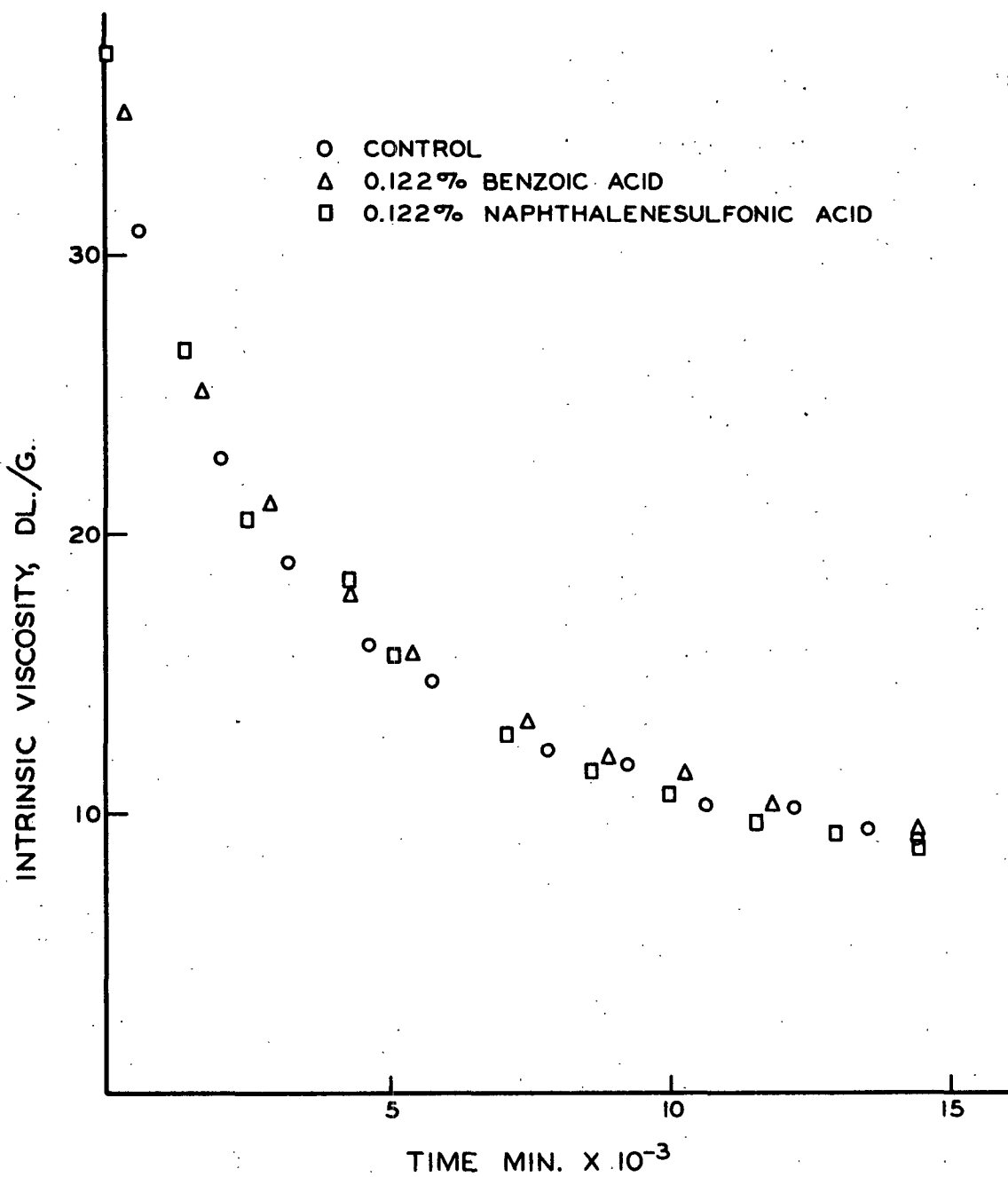


Figure 3. Effect of Free-Hydroxyl Couplers on the Depolymerization of Alkali Cellulose

(Experiment 9)

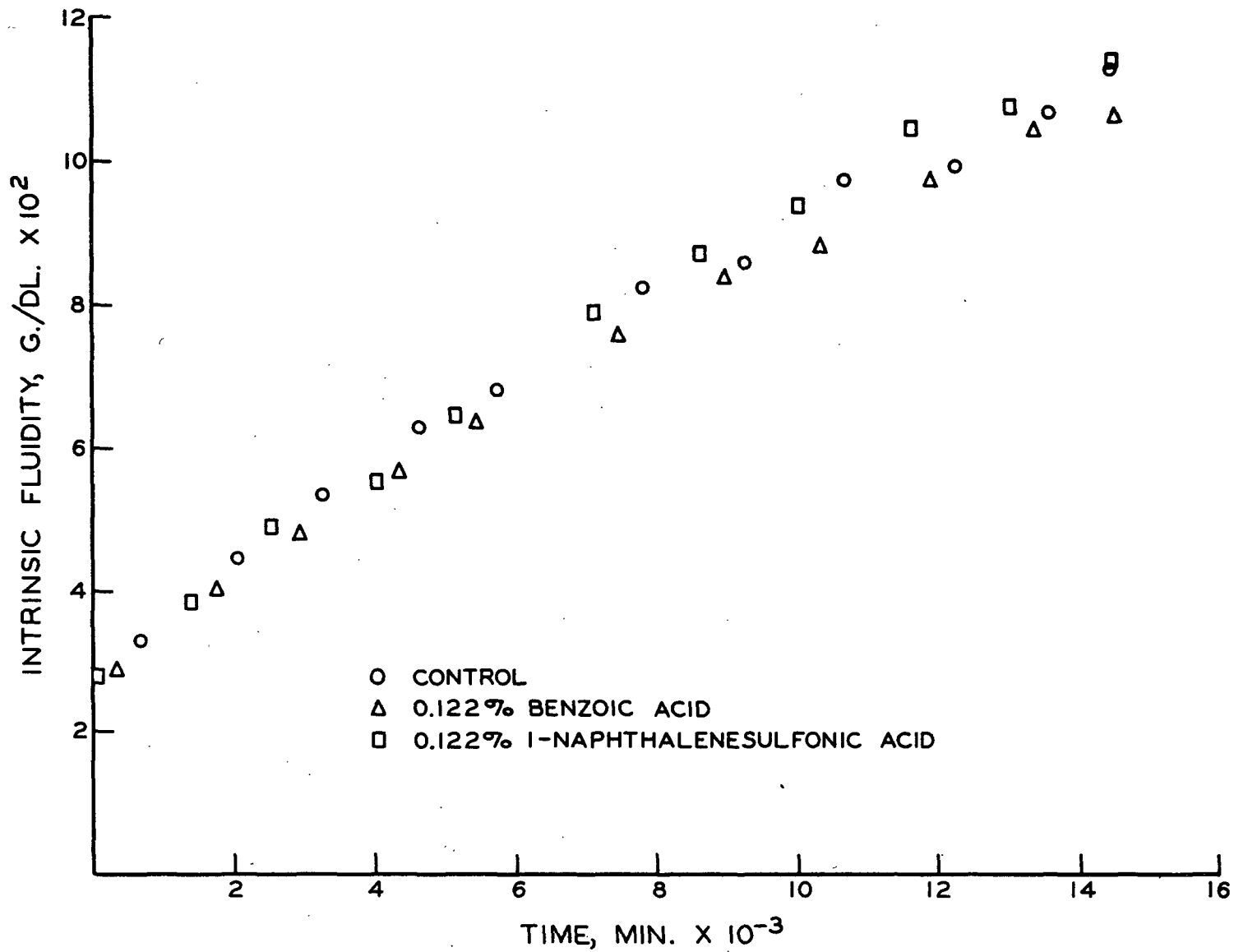


Figure 4. Effect of Free-Hydroxyl Couplers on the Fluidity of Alkali Cellulose

(Experiment 9)

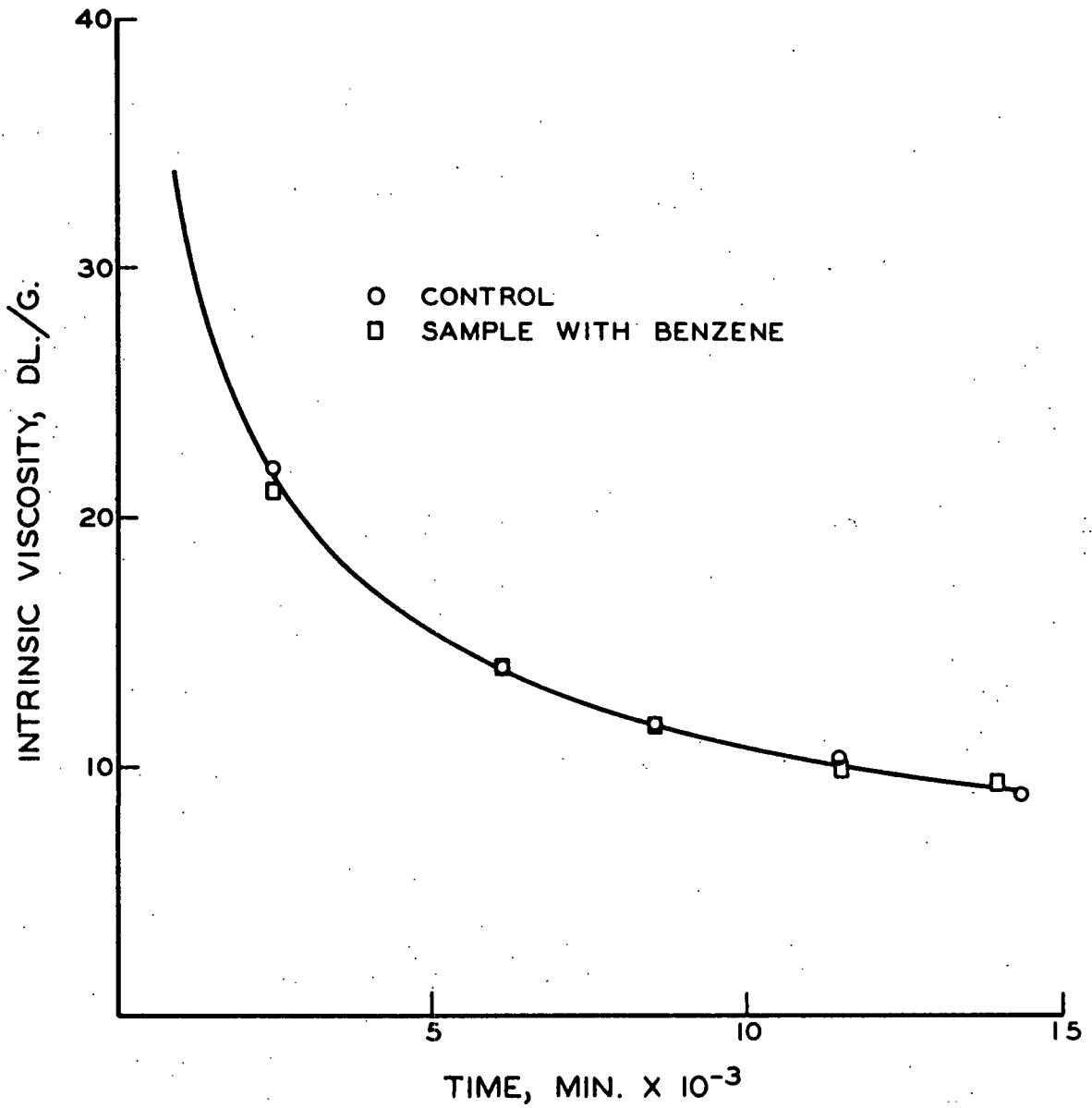


Figure 5. Effect of Benzene on the Depolymerization of Alkali Cellulose

(Experiment 10)

there is no cumulative effect of nitrogen buildup in the flask; an effect which would slow down autoxidation. This conclusion is of importance to the phenol production study; for if such inhibition had occurred, it would have suppressed the production of free hydroxyl radicals, and have given the low phenol yield.

The effect of benzene on the depolymerization of alkali cellulose was studied in Experiment 10. (The samples of cellulose for intrinsic viscosity determination were regenerated from the alkali cellulose of Experiment 6.) The results (Fig. 5) show that there is no effect, and except for the high initial intrinsic viscosity, are identical to those of the other free hydroxyl couplers shown in Fig. 3. The two samples were identical except for the benzene, which accounts for the almost perfect duplication of the control run with the one containing benzene.

It has been clearly demonstrated that benzene, benzoic acid, and 1-naphthalenesulfonic acid do not interfere with the reactions of alkali cellulose autoxidation that cause the breakdown of the cellulose molecule. Since these substances would react with free hydroxyl radicals, this free radical is not a likely intermediate in these depolymerization reactions.

PHENOL AS AN INHIBITOR

The effect of phenol as an inhibitor has also been studied. Phenol is known to be an antioxidant in the autoxidation of olefinic hydrocarbons (62), blocking two kinetic chains per molecule of phenol consumed. At the beginning and end of the aging period of the phenol stability study, reported in Appendix III, samples of cellulose were regenerated from the alkali cellulose for the purpose of viscosity determination. The results can be seen in Table V.

TABLE V

EFFECT OF 0.004% PHENOL CONCENTRATION
ON THE AGING OF ALKALI CELLULOSE

	Intrinsic Viscosity	
	Initial	Final
"Phenol" sample, dl./g.	32.8 ^a	7.9
		<u>7.9</u>
Av., dl./g.	32.8	7.9
Control sample, dl./g.	33.4	7.7
		<u>7.7</u>
Av., dl./g.	33.4	7.7

^adl./g. is deciliters per gram.

The observed difference (0.2 dl./g.) is believed to be insignificant in view of the usual behavior of phenol as an inhibitor of free radical chain reactions. Entwistle, Cole, and Wooding (26) also report that phenol does not inhibit alkali cellulose autoxidation.

It has been demonstrated, therefore, that a general inhibitor of free radical reactions, phenol, does not inhibit alkali cellulose autoxidation.

PHOTOCATALYSIS STUDY

The photocatalytic behavior of alkali cellulose autoxidation was studied in Experiment 11, the results of which are given in Table VI.

The rate of alkali cellulose autoxidation is remarkably insensitive to light as can be seen from Table VI. No significant difference in viscosity was noted between the samples aged for 10 days in the dark and in the light. Any effect, whether inhibitory or acceleratory, would have been cumulative, so the method should have been a very sensitive indication of photocatalysis. The absence of

photocatalysis in the autoxidation of alkali cellulose is very good evidence that it is not a free radical reaction.

TABLE VI
PHOTOCATALYSIS STUDY
(Experiment 11)

Cellulose	See Appendix II, Method B
Alkali strength	5M NaOH
Consistency of alkali cellulose	26.42% o.d. cellulose
Amount of alkali cellulose in each cell	64 g.

Cell diameter	150 mm.
Illumination type	"Daylight" Fluorescent
Illumination intensity -top	13 ft.-candles
-bottom	3.2 ft.-candles
Duration of aging	12,690 minutes

Temperatures:

Time, min.	Dark Cell, °C.	Light Cell, °C.
120	34.0	33.9
1950	34.3	34.3
4140	31.3	30.8
5580	31.7	31.7
7065	31.8	31.5
8955	32.9	32.8
9890	30.9	30.5
12,690	30.6	30.2
Mean temperature	32.2	32.0

Intrinsic viscosities:

	Dark	Light
initial, dl./g.	110.0	110.0
final, dl./g.	9.4	9.3
	9.5	9.3
	<u>9.6</u>	<u>9.5</u>
mean	9.5	9.4

ELECTRON PARAMAGNETIC RESONANCE

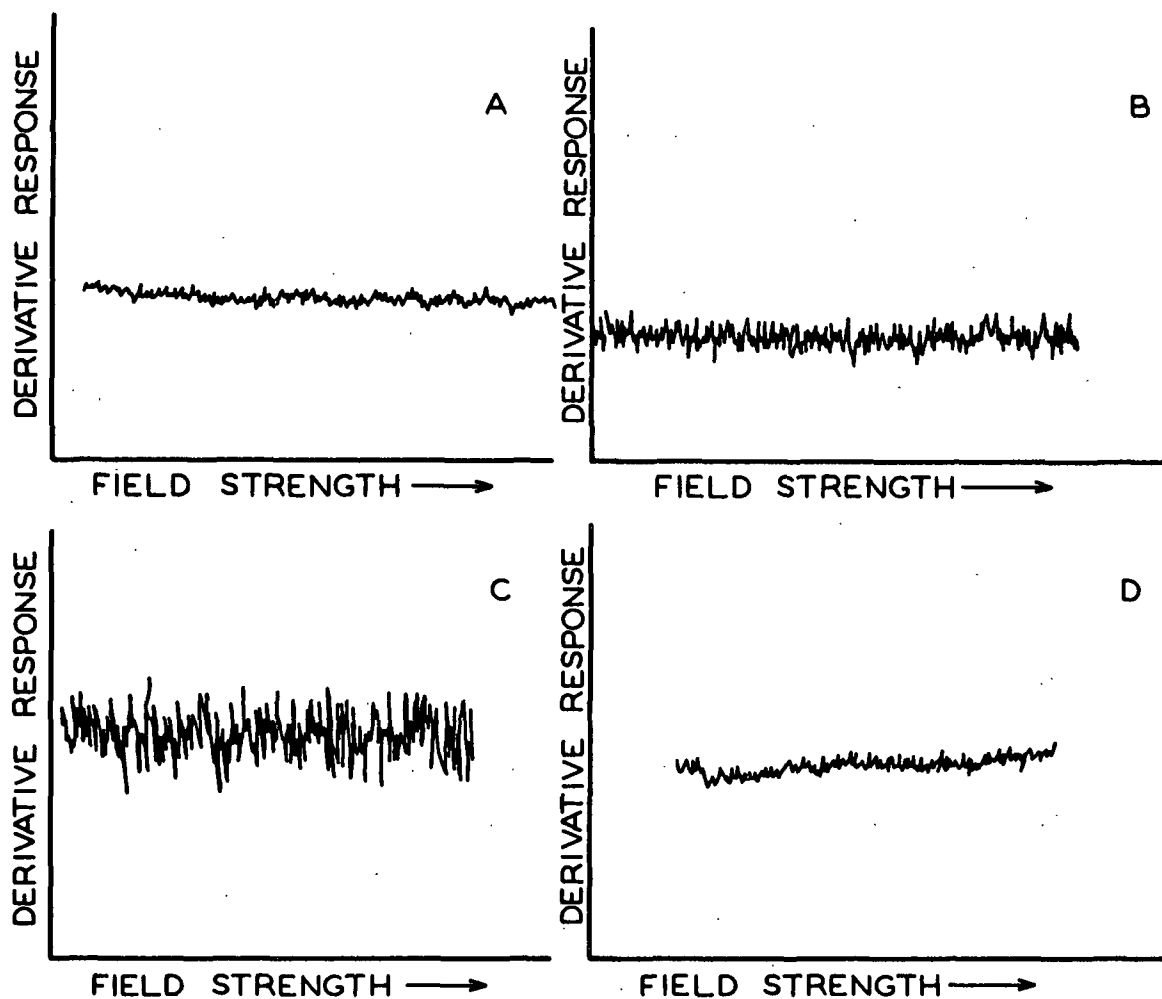
EPR spectra of alkali cellulose were obtained at room temperature (25°C.) and at about -150°C.

The spectra of alkali cellulose at room temperature were determined on the alkali cellulose in a fused silica tube. As fused silica is free of resonance in the EPR region, a very clear picture of the resonances of unpaired electrons in the sample should have been obtained. There were absolutely no resonances observed at any setting of the Varian spectrometer. The alkali cellulose used in this experiment had aged for about 40 hours (see Fig. 6).

Greater sensitivity is sometimes obtained when samples are frozen. Samples of freshly prepared and of aged alkali cellulose, which had been frozen in dry ice were compared. Unfortunately, these tests were conducted in pyrex tubes which gave a complex spectrum when empty, indicating the presence of transition elements that were present in the glass, and also a free radical.

The results are summarized in Fig. 7. These spectra were obtained using the maximum sensitivity of the spectrometer for free radical resonance. The top two curves of Fig. 7 are reproductions of the actual spectra that were obtained for the unaged alkali cellulose. The spectrum of the empty pyrex tube was graphically subtracted from the pyrex tube which contained alkali cellulose, the resulting difference curve being shown. The same thing was done for the alkali cellulose sample that had been aged for 55 hours. The peak to the right is a residual response of the free radical in the pyrex tube that did not cancel upon subtraction. The peak to the left is a free radical in the alkali cellulose.

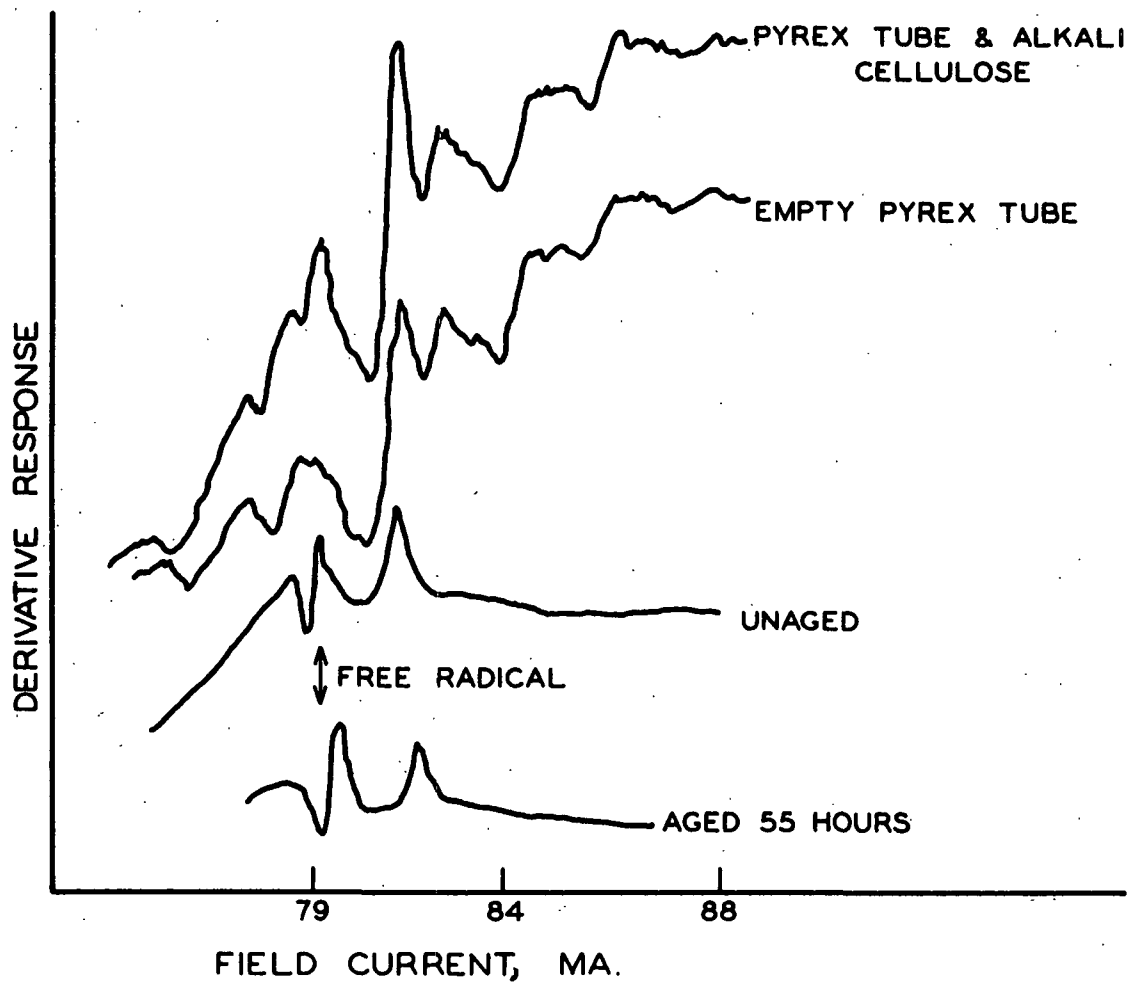
The peak observed is very weak, and does not change appreciably from unaged to aged alkali cellulose. This is an entirely different picture than would have



INSTRUMENT SETTINGS:

	A	B	C	D
GAIN	400	1000	2000	400
MODULATION	500	50	50	5000
POWER, db	-10	-10	-20	-20
SWEEP RATE	3 X 2	3 X 2	3 X 2	3 X 2
RECORDER RESPONSE	2	2	2	2

Figure 6. EPR Spectra of Autoxidizing Alkali Cellulose at Room Temperature Using Silica Tubes



INSTRUMENT SETTINGS: BOTH SAMPLES
GAIN 200
MODULATION 2000
POWER, db -20
SWEEP RATE 4 X 2
RECORDER RESPONSE 2

Figure 7. EPR Spectra of Autoxidized Alkali Cellulose at $-150^{\circ}\text{C}.$, Using Pyrex Tubes

been expected if a free radical mechanism were operating. A very elaborate and strong spectrum would be expected (63), and from the steps of the free radical mechanism, it was predicted that the spectra for freshly prepared alkali cellulose would be quite different than for aged alkali cellulose.

It is possible, however, that the free radical concentrations involved in the autoxidation are simply too low to detect, although sufficient to account for the reactions involved. There are also situations in which free radicals are not detected by EPR because the resonances are too broad. Therefore, the results of this experiment are not conclusive, but they do show that present EPR techniques do not detect the expected amount of free radicals in autoxidizing alkali cellulose. Reference was made to the fact on p. 20 that the EPR technique is sensitive to 10^{-6} to 10^{-8} moles of unpaired spins per gram of material; free radicals could have been present at even lower concentrations.

A POSTULATED MECHANISM FOR
ALKALI CELLULOSE AUTOXIDATION

The experimental evidence from this work, and the theoretical considerations previously discussed, have indicated that alkali cellulose does not autoxidize by a free radical mechanism. It is important that the facts of alkali cellulose autoxidation be reconsidered, and new possibilities explored for a mechanism.

It is difficult to abandon any concept, such as the free radical mechanism, without a more comprehensive alternative. The ionic mechanism postulated here is such an alternative. It is more consistent with the many observed facts of the reaction than is the free radical mechanism.

THE INITIATION STEP: PEROXIDE FORMATION

It is known from the work of Entwistle, Cole and Wooding (7) that the initial rate of oxygen consumption is proportional to the reducing power of the cellulose, as measured by the copper number. Furthermore, the initial oxygen consumption rate is in many cases much higher than the steady-state reaction rate. Initially, then, oxygen reacts spontaneously with some functional group that is related to the copper number. This functional group is undoubtedly an aldehyde group.

There are ordinarily two classes of reactions for aldehyde groups in alkali media. The aldol condensation reaction occurs whenever α -hydrogens are available, but in compounds where the α -hydrogen is lacking a Cannizzaro reaction will occur. Since these reactions are both bimolecular with respect to the aldehydes, neither would be likely (except internally as a rearrangement) if the aldehyde group was attached to a cellulose molecule. If cellulosic aldehydes (XVI) were placed in a strongly alkaline medium, they would therefore form the Cannizzaro intermediates shown by formulas XVII and XVIII.

have shown this to be a complex reaction (69-71). Kleinert has shown, however, that there is one rupture of the cellulose chain for every perhydroxyl ion that reacts with cellulose in alkaline media (72).

Therefore, the proposed propagation step is attack of the cellulose by the perhydroxyl ion, producing two cellulosic fragments. The reason for the randomness of attack is that the perhydroxyl ion is produced in situ, and is free to migrate in the highly swollen cellulose.

A variety of possible reactions exist for the actual attack of perhydroxyl ion on cellulose. It is not a reaction of any marked specificity. However, the following possible modes of attack may be cited.

1. Nucleophilic substitution at the glycosidic linkage by the perhydroxyl ion.

At room temperature the glycosidic linkage is quite stable to hydroxyl ion. However, Wiberg (94) has reported that perhydroxyl ion is 10^4 times as reactive in the hydrolysis of benzonitrile as is the hydroxyl ion. Other reports also illustrate the strongly nucleophilic character of perhydroxyl ion (95).

2. Substitution of a hydroxyl on an anhydroglucose unit.

Due to the nucleophilic nature of the perhydroxyl ion, it could substitute any of the three hydroxyl groups on the anhydroglucose unit. This would lead to subsequent decomposition in the alkaline medium.

3. Simple oxidations.

Peroxide attack could occur through oxidations of any hydroxyl to a carbonyl group. Alkaline degradation would be likely to occur regardless of the point of attack (96).

AUTOCATALYSIS

In many cases, an oxidized cellulose is more strongly reducing than an unoxidized cellulose. This almost paradoxical behavior occurs when the oxidant produces aldehyde groups, which are further oxidized by the reagent used in the reducing-value determination. This phenomenon could easily explain the autocatalysis of alkali cellulose autoxidation; for the attack on cellulose by the perhydroxyl ion could generate new reducing groups. There is evidence, as will be seen, that considerably more than one reducing group may be produced at a break in the cellulose molecule during oxidative alkaline degradation.*

First of all, Lidman-Safwat and Theander (73) have compared copper-number measurements with carbonyl content, as measured by borohydride reduction. Up to 12 times as many equivalents of copper were reduced as there were equivalents of carbonyl present.

Colbran and Davidson (67) compared the number of moles of copper reduced during the copper number measurement (Braidy method) to the number of moles of carboxyl formation on the cellulose. This was done on hydrocelluloses. The results suggested that the Braidy copper-number reagent oxidized the reducing end of the hydrocellulose molecule in a complex way until stability towards the oxidant was attained by the formation of a terminal carboxyl group, and that an average of 22 atoms of copper were reduced, or 11 atoms of oxygen consumed, before stability was achieved.

An experiment has been conducted in this thesis to measure how many cupric ions are reduced to cuprous ion at a single chain break during the copper number

* This happens because of fragmentation and peeling reactions originating from the point at which the break occurs.

measurement. The procedure was as follows. A sample of cellulose was boiled in dilute alkali until it had nearly zero copper number and all alkali-sensitive linkages were broken. Two samples (A and B) were lightly oxidized as described on p. 33. Copper numbers were run on the samples. The residual cellulose from the copper number analysis was washed and dried.

Next, an aliquot of the alkali-boiled sample and portions of the residual celluloses from the copper number determinations were nitrated, and the number-average molecular weights determined by osmometry. From a comparison of the copper numbers with the change in molecular weight, the equivalents of electrons involved in reducing copper per chain break was inferred. This value was calculated from the following equation:

$$N = (C/63.54 \times 2) / (100/\underline{Mn}_2 - 100/\underline{Mn}_1) \quad (30)$$

where:

- \underline{N} = Equivalents of electron pairs transferred per rupture.
- \underline{C} = Copper number, the number of grams of copper that are reduced from the +2 to +1 state per 100 g. of cellulose.
- \underline{Mn}_1 = Number average molecular weight of original sample.
- \underline{Mn}_2 = Number average molecular weight of sample after copper number determination.

The numerator of Equation (30) is the number of electron pairs transferred from the cellulose to the copper reagent per hundred grams of cellulose, during the copper number measurement. The denominator is the number of end-groups involved during the copper number measurement.

The data and results are given in Table VII.

TABLE VII

DATA AND RESULTS OF COPPER-NUMBER STUDY

Unoxidized Cellulose

Copper number ^a	0.003
Number-average molecular weight	272,000

Oxidation

Type	Hypochlorite, pH 6
------	--------------------

Copper numbers^a

Sample A (average of 4 runs)	1.99
Sample B (average of 4 runs)	0.633

Number Average Molecular Weights after Copper-number
Determination

Sample A	88,700
Sample B	138,600

Results

	Electron Pairs Transferred per Rupture
Sample A	20
Sample B	14

^aMethod of Clibbens and Geake (74).

The results show that from 14 to 20 electron pairs are transferred from the cellulose to the copper reagent during the copper number measurement. This compares favorably with the 11 electron pairs reported by Colbran and Davidson (67). Oxidative alkaline degradation can therefore be visualized as a complex series of rearrangements resulting from a break in the cellulose molecule, with the formation of many reducing groups. Oxidation of these groups by either cupric

ion or oxygen will occur as they are formed; the reaction will stop when a carboxylic acid structure is formed which is stable to alkaline rearrangement.

It is proposed that alkali cellulose autoxidation is autocatalytic by virtue of this phenomenon. Namely, one perhydroxyl ion reacts with cellulose causing an alkali-sensitive linkage. The reducing groups produced during the subsequent alkaline rearrangements react with oxygen to produce many perhydroxyl ions.

TERMINATION: PEROXIDE DECOMPOSITION

There are many things that could happen to moderate the rate of the cyclic reaction sequence that has been proposed. Hydrogen peroxide is not stable in alkali, and undergoes slow decomposition to oxygen and water. Hydrogen peroxide would also react with low-molecular weight fragments from cellulose degradation.

It is particularly interesting that silver, gold (26) and lead (23) are strong negative catalysts to alkali cellulose autoxidation. Silver also reduces the peroxide content of alkali cellulose to zero (26). According to Schumb, et al. (75), these three metals all act as catalysts for hydrogen peroxide decomposition. Of these metals, silver is particularly active.

COMPARISON OF THE PEROXIDE MECHANISM TO EXPERIMENTAL OBSERVATIONS

In the introduction a list of the known facts of alkali cellulose autoxidation was made. It is rewarding to note that the peroxide mechanism seems to be in harmony with these facts. They will be discussed in the same order as previously presented.

1. Alkali cellulose autoxidation proceeds only under strongly alkaline conditions.

The peroxide mechanism demands that conditions be strongly alkaline for three reasons. First, the rate of peroxide formation from the Cannizzaro intermediate would be proportional to the hydroxide ion concentration. Secondly, peroxide attack of cellulose is enhanced by strongly alkaline conditions. Finally, cellulose undergoes fragmentation reactions in alkali, which accounts for autocatalysis.

2. Autoxidation occurs only in pressed alkali cellulose.

At low consistencies the perhydroxyl ion is undoubtedly still formed, but it suffers severe dilution by the large bulk of the liquid phase. Since the attack on cellulose by the perhydroxyl ion would be proportional to peroxide concentration, this reaction would be very slow. The amount of peroxide decomposition at any given peroxide concentration would increase in proportion to the amount of liquid present. Thus, we would predict that autoxidation would be spontaneous only above a certain cellulose-to-alkali ratio. This is analogous to "critical" concentrations in any self-propagating process.

3. Oxygen consumption is a phenomenon interrelated with depolymerization.

The mechanism demands that oxygen be converted to perhydroxyl ion, which then attacks cellulose, causing depolymerization.

4. The initial oxygen consumption rate is proportional to the copper number reducing value of the regenerated cellulose.

The initiation reaction proposed for the peroxide mechanism is based on this observation.

5. Oxygen is consumed at a constant rate after about 24 hours of aging.

The spontaneous decomposition of the perhydroxyl ion would be bimolecular. The rate of decomposition would increase very rapidly as the concentration increased, which would exert a moderating effect on the autoxidation rate.

6. Oxygen pressure is not rate-controlling in the range of conditions usually encountered.

Probably the rate of peroxide attack or the rate of reducing group formation is rate controlling. A thorough kinetic analysis of the system would be required to elucidate such a fine point as this. It would primarily involve a study of peroxide formation rate, rate of peroxide attack on the cellulose and rate of reducing group production.

7. Transition elements act as catalysts to alkali cellulose autoxidation.

The interesting observation concerning the negative catalysis of gold, silver and lead was mentioned on p. 67. The catalysis mechanism of positive catalysts, such as manganese, iron and cobalt is not known, but these substances could act through oxidative attack on the cellulose, followed by their reoxidation by perhydroxyl ion. This would be in agreement with the observation that positive catalysts do not affect the initial rate of oxygen absorption, but exert their influence on the rate at steady-state conditions. It is significant that these substances do not catalyze the decomposition of peroxides in alkaline media as do the negative catalysts (75).

8. Both positive and negative catalysts lower the peroxide content of alkali cellulose.

Positive catalysts would catalyze the reaction between the perhydroxyl ion and cellulose, negative catalysts, the decomposition reaction of the perhydroxyl ion. Both of these reactions would result in a lowering of the perhydroxyl ion concentration.

9. Many of the organic antioxidants which inhibit free radical autoxidations slow down the rate of alkali cellulose autoxidation.

Many such antioxidants are also compounds that can be easily attacked by relatively weak oxidants. These substances might react with hydroperoxyl ion slowly and give the retarding effect that has been noted. Phenol and naphthol, although good inhibitors of free radical autoxidations, are poor inhibitors of alkali cellulose autoxidation. These substances are probably less reactive with the perhydroxyl ion than are more strongly reducing antioxidants, such as hydroquinone. Sodium thiocarbonate has been mentioned as being a powerful inhibitor of alkali cellulose autoxidation (33). Mellor reports that sodium thiocarbonate reacts vigorously with oxygen (47), and undoubtedly can reduce the perhydroxyl ion with ease.

10. Positive catalysts increase the amount of depolymerization that occurs for a given amount of oxygen consumed; negative catalysts decrease the amount of depolymerization for a given amount of oxygen consumption.

If catalysts behave in the way just described in Point 8, it would explain this behavior. By catalyzing the reaction between the perhydroxyl ion and cellulose, the efficiency of the depolymerization process would be improved at the expense of peroxide decomposition. Negative catalysts would lower the relative amount of cellulose attack if they catalyzed peroxide decomposition.

11. Hydrogen peroxide is always present during autoxidation, in very low concentration.

This fact is the key to the whole mechanism. Since the perhydroxyl ion attacks cellulose under alkaline conditions, cellulose decomposition must be occurring as long as it is present. The perhydroxyl ion must be in continual production, otherwise it would soon disappear.

12. Approximately one carboxyl group is formed in aged alkali cellulose per residual cellulose chain.

This carboxyl group probably forms at the termination of the fragmentation sequence ("peeling" and "stopping" reactions) after cellulose has been attacked. The studies of Colbran and Davidson (67) and the results in this thesis on the copper number indicate that one carboxyl group is formed at the termination of the peeling sequence. Otherwise, these studies would not have given values of reducing group production that were in such close agreement, for the former study was based on the carboxyl content, and the latter was based on the amount of rupture that occurred.

13. The carbonyl content does not vary appreciably with aging time.

This observation is consistent with the peroxide mechanism. Since the rate of oxygen consumption becomes constant after the first 24 hours and is proportional to the carbonyl content, it would follow that the carbonyl content would reach a fixed value at steady-state conditions.

14. Considerable amounts of carbon dioxide are produced by the autoxidation reaction.

Fragmentation reactions that occur in strong alkali would be likely to lead to carbon dioxide formation through decarboxylation.

15. The degradation that accompanies alkali cellulose autoxidation is a very random process.

The molecular weight distribution curves for aged alkali cellulose and cellulose degraded by hydrogen peroxide are quite similar (72, 83, 87), the aged alkali cellulose exhibiting slightly narrower distribution. This is exactly as would be expected from the peroxide mechanism; both reactions proceed by the same chemical attack at new sites on the cellulose, but in the case of aging the reaction is very slow, and the perhydroxyl ion very uniformly distributed in the alkali cellulose.

SUGGESTED FUTURE WORK

The methods to be outlined should yield important information about the autoxidation reaction of alkali cellulose regardless of mechanism, but of course are concerned with aspects of the peroxide mechanism. No simple, clear-cut experiment has yet been conceived that will prove or disprove the peroxide mechanism.

1. A thorough kinetic study of the reaction could be conducted.

So far, the attempts to analyze the kinetics of autoxidizing alkali cellulose have been disappointing. The most comprehensive study has been conducted by Schulz and Mertes (31), but they had no specific reaction possibilities. A thorough kinetic analysis of the peroxide mechanism could be worked out, relating oxygen consumption, reducing-group content, perhydroxyl ion content and rate of cellulose decomposition with time. No one has analyzed this reaction in terms of a cyclic reaction sequence.

2. An investigation could be made of a possible correlation between the ability of substances to catalyze the decomposition of, or react with, hydrogen peroxide and the ability of these substances to inhibit alkali cellulose autoxidation.

This study would confirm or deny the explanation offered by the peroxide mechanism for the behavior of negative catalysts. Some consistent method of evaluating the catalytic influences of these substances in terms of the reactions would be needed. For example, the time required to reduce a given amount of peroxide to half its value could be used as an evaluation of the ability of a substance to decompose hydrogen peroxide. The effect of the substance on the autoxidation rate of alkali cellulose (in terms of oxygen consumption or rate of bond breaking of the cellulose) would also be a useful study. If these substances inhibit alkali cellulose autoxidation by virtue of their action

on the perhydroxyl ion that is present, a plot of these two effects should yield a single curve for all substances and concentrations.

3. Determine to what extent cellulose degradation during aging is due to perhydroxyl attack.

First, a rate study of perhydroxyl ion attack on cellulose would be conducted. The results should be expressed as rate of degradation at given perhydroxyl ion concentrations. Next, the perhydroxyl ion concentration and the rate of degradation of autoxidizing alkali cellulose at steady-state conditions would be determined. Calculations would show to what extent the degradation that accompanies autoxidation is due to perhydroxyl ion attack on cellulose.

This would be a difficult but worthwhile study. Oxygen would have to be excluded from the system while the rate of perhydroxyl ion attack was being studied, and the spontaneous decomposition of the peroxide would have to be contended with. If the degradation of alkali cellulose is due solely to hydroperoxyl ion attack, it is a strong point in favor of the peroxide mechanism.

4. A study of the reaction of aldehyde groups which are attached to a high-polymer structure should be conducted.

It would be desirable to conduct a study of the reactions of aldehyde groups that are not free to undergo bimolecular reactions. A model high-polymer aldehyde is needed to replace cellulose in this study, for cellulose is much too reactive with by-products (such as perhydroxyl ion) that might be formed. A suggestion for such a model compound would be polyacrylic acid, subjected to varying degrees of reduction with lithium aluminum hydride. It would be of great importance to the peroxide mechanism to see if this polymer would react with oxygen under alkaline conditions to form perhydroxyl ions.

5. A study of peroxide production from cellulose in a slurry should be conducted.

With a very sensitive analysis for hydrogen peroxide, the peroxide production at lower and lower consistencies of cellulose in alkali could be determined. As infinite dilution was approached, the amount of hydrogen peroxide production should approach some constant value that would be proportional to the reducing power of the cellulose. The peroxide method of Schales (38) or of Perschke and Broda (41) could be used.

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APPENDIX I

TABULATED DATA

TABLE VIII

OXYGEN CONSUMPTION MEASUREMENTS

Control Runs:

1. First Control Run (Experiment 8)

Cellulose used	Hypochlorite-oxidized linters
Consistency of alkali cellulose	30.42% o.d. cellulose
Temperature of run	30°C.
Oxygen pressure	495.9 mm. Hg.

Absorption data:

Time, min.	ml. O ₂ /min. x $\frac{dv}{dt}$, g. cellulose ^a
15	0.00458
45	0.00406
117	0.00316
211	0.00242
335	0.00177
526	0.00132
697	0.00106
1276	0.00093
1462	0.00077
2070	0.00067

^aThe volume of oxygen is calculated at a temperature of 0°C. and at a pressure of 760 mm. of mercury.

\underline{v} = volume

\underline{t} = time

TABLE VIII (continued)
OXYGEN CONSUMPTION MEASUREMENTS

2. Second Control Run (Experiment 8)

Cellulose used	Hypochlorite-oxidized linters
Consistency of alkali cellulose	28.40% o.d. cellulose
Temperature of run	30°C.
Oxygen pressure	495.5 mm. Hg

Absorption data:

Time, min.	$\frac{dv}{dt},$ ml. O ₂ /min. x g. cellulose ^a
40	0.00485
83	0.00398
152	0.00316
271	0.00227
392	0.00173
550	0.00133
1245	0.00080
1760	0.00075
2790	0.00078
2861	0.00077
3458	0.00075
4270	0.00080

^aThe volume of oxygen is calculated at a temperature of 0°C. and at a pressure of 760 mm. of mercury

\underline{v} = volume

\underline{t} = time

TABLE VIII (continued)

OXYGEN CONSUMPTION MEASUREMENTS

Benzoic Acid Run (Experiment 8)

Cellulose used	Hypochlorite-oxidized linters
Consistency of alkali cellulose	30.29% o.d. cellulose
Temperature of run	30°C.
Oxygen pressure	499.4 mm. Hg
Amount of benzoic acid	0.027% on alkali cellulose

Absorption data:

Time, min.	ml. O ₂ /min. x $\frac{dv}{dt}$, g. cellulose ^a
33	0.00316
105	0.00281
183	0.00237
304	0.00159
530	0.00130
585	0.00121
1330	0.00081
1433	0.00083
1732	0.00075
1945	0.00072
2874	0.00076
3148	0.00076
3572	0.00073
4610	0.00070
4950	0.00072
5776	0.00072
7160	0.00068
8500	0.00070
9173	0.00072

^aThe volume of oxygen is calculated at a temperature of 0°C. and at a pressure of 760 mm. of mercury.

\bar{v} = volume

\bar{t} = time

TABLE VIII (continued)
OXYGEN CONSUMPTION MEASUREMENTS

1-Naphthalenesulfonic acid run (Experiment 8)

Cellulose used	Hypochlorite-oxidized linters
Consistency of alkali cellulose	28.40% o.d. cellulose
Temperature of run	30°C.
Oxygen pressure	495.5 mm. Hg
Amount of 1-naphthalene-sulfonic acid	0.053%

Absorption data:

Time, min.	$\frac{dy}{dt},$ ml. O ₂ /min. x g. cellulose ^a
14	0.00479
90	0.00400
198	0.00301
328	0.00223
415	0.00184
480	0.00162
970	0.00094
1065	0.00090
1125	0.00087
1250	0.00087
1360	0.00082
1526	0.00085
1791	0.00079
2453	0.00079
2850	0.00079
3133	0.00077
4480	0.00080

^aThe volume of oxygen is calculated at a temperature of 0°C. and at a pressure of 760 mm. of mercury.

\bar{v} = volume

\bar{t} = time

TABLE IX

EFFECT OF AROMATIC SUBSTANCES ON THE DEPOLYMERIZATION
OF ALKALI CELLULOSE

(Experiment 9)

General Data

Cellulose used	See Appendix II, Method C
Alkali strength	5M NaOH
Temperature	30°C.

Composition of Samples

Sample	Total Alk. Cell., g.	O.D. Cell., %	Wt. O.D. Cell., g.	Aromatic Substances, %
a. Control	336	26.96	90.5	none
b. Benzoic acid	313	31.34	98.1	0.122 ^a
c. 1-Naphtha- lenesulfonic acid	347	27.43	95.2	0.122 ^a

^aBased on alkali cellulose.

TABLE IX

EFFECT OF AROMATIC SUBSTANCES ON THE DEPOLYMERIZATION
OF ALKALI CELLULOSE

(Experiment 9)

Intrinsic Viscosity Data

a. Control

Time, min.	$[\eta]$, dl./g.	$1/[\eta]$, g./dl.
607	30.7	0.0326
2055	22.6	0.0443
3260	18.9	0.0529
4680	16.0	0.0625
5795	14.7	0.0680
7810	12.2	0.0819
9260	11.7	0.0854
10650	10.3	0.0972
12210	10.1	0.0991
13635	9.4	0.1063
14435	8.9	0.1123

b. Benzoic acid

Time, min.	$[\eta]$, dl./g.	$1/[\eta]$, g./dl.
345	35.0	0.0286
1725	25.0	0.0400
2930	21.0	0.0477
4350	17.8	0.0562
5460	15.7	0.0637
7480	13.3	0.0753
8930	12.0	0.0833
10320	11.4	0.0878
11880	10.3	0.0971
13305	9.6	0.1041
14460	9.4	0.1063

c. 1-Naphthalenesulfonic acid

Time, min.	$[\eta]$, dl./g.	$1/[\eta]$, g./dl.
35	37.0	0.0271
1410	26.5	0.0377
2615	20.5	0.0488
4035	18.0	0.0549
5145	15.6	0.0641
7165	12.8	0.0782
8615	11.5	0.0870
10005	10.7	0.0935
11565	9.6	0.1041
12990	9.3	0.1075
14400	8.8	0.1136

TABLE X

EFFECT OF AROMATIC SUBSTANCES ON THE DEPOLYMERIZATION
OF ALKALI CELLULOSE

(Experiment 10)

General Data

Cellulose used	See Appendix II, Method A
Temperature	30°C.
Alkali strength	5M NaOH

Composition of Sample

Sample	O.D. Cell, %	Amount of Benzene, ml.
Control	26.34	none
Benzene	26.34	5

Intrinsic Viscosity Data

Time, min.	[η], dl./g.		1/[η], g./dl.	
	Control	Benzene	Control	Benzene
15	59.0	59.0	0.0170	0.0170
2505	22.0	21.1	0.0455	0.0474
6105	14.0	14.1	0.0714	0.0709
8565	11.7	11.8	0.0855	0.0848
11475	10.3	9.9	0.0972	0.1010
13995	--	9.3	--	0.1075
14385	8.9	---	0.1123	--

APPENDIX II

METHODS OF PURIFYING CELLULOSE

In all cases, the starting material was acetate-grade cotton linters, obtained from Buckeye Cellulose Corporation. This material was in the sheet form.

METHOD A. This method consisted of a 3-stage purification.

Stage I. A 105-g. sample of linters, air-dry weight, was boiled for 4 hours in 1/3% sodium chlorite solution. The cooking liquor consisted of 10 grams of sodium chlorite, technical grade, dissolved in 3 liters of distilled water, with the pH adjusted to 4.0 with acetic acid. The cellulose was washed with redistilled water after cooking until the washings were free of chlorite, as determined by starch-iodide test paper.

Stage II. The cellulose was boiled for 5 hours in 3 liters of redistilled water containing 150 g. of reagent-grade sodium hydroxide. It was washed with redistilled water until the washings were neutral to phenolphthalein.

Stage III. The wet stage II cellulose was rinsed with 500 ml. of 5M sodium hydroxide solution to displace water. It was then placed in a beaker with 1500 ml. of 5M sodium hydroxide and steeped for 12 hours at room temperature. The sodium hydroxide solution was made up from reagent-grade sodium hydroxide and redistilled water. The alkali cellulose was then washed to neutrality with redistilled water. It was necessary to break up lumps of alkali cellulose with a Waring Blendor twice during the washing step in order to aid alkali removal. The cellulose was dried in a circulating oven at 105°C.

METHOD B. This method consisted of a simple dilute alkali boil.

A 60 to 70-gram sample of linters, air-dry weight, was placed in 2 liters of 5% sodium hydroxide solution. The sodium hydroxide solution was prepared from reagent-grade sodium hydroxide and ordinary distilled water. After 7 hours of boiling the cellulose was washed free of alkali, and dried in a circulating oven at 105°C.

METHOD C. This method consisted of a series of organic-solvent extractions.

Six-hundred grams of linters were cut into 6-inch squares and soaked in water to swell the fibers. The water-swollen cellulose was given 3 acetone extractions, one 20:80 acetone-chloroform extraction, and then 6 chloroform extractions, in that order. These extractions were accomplished by allowing the cellulose squares to act as sponges, absorbing solvent until they were saturated; then they were pressed in a stack on a 6 by 6-inch press with about 8 tons pressure.

The pads were spread to air dry, then slurried in water by means of a Waring Blendor. The slurried cellulose was given two successive boils in 2% sodium hydroxide solution of 3 and 4 hours each, respectively. The sodium hydroxide solution was prepared from reagent-grade sodium hydroxide and ordinary distilled water.

The next step was to remove metal ions (92). The cellulose was boiled for 20 minutes in 12 liters of water (pH 3.0 with acetic acid) containing 80 milligrams of ethylenediaminetetraacetic acid. The cellulose was washed to neutrality with distilled water and oven-dried at 105°C.

APPENDIX III

PHENOL EXTRACTION PROCEDURE

The method used in this work for the isolation of microgram quantities of phenol from alkali cellulose was in part an adaptation of a screening procedure from Standard Methods for the Examination of Water, Sewage and Industrial Wastes (64)

EXTRACTION OF PHENOL FROM AQUEOUS SOLUTION

In the x-ray studies on water and on 5M sodium hydroxide, with benzene, the phenol was isolated and concentrated using an ether extraction. The following experiment was conducted to evaluate the efficiency of this extraction.

An aqueous solution of phenol was prepared of known concentration. One liter was taken, and the pH adjusted to between 3 and 4 with 8.5% phosphoric acid solution.

This phenol solution was extracted 4 times with 40-ml. portions of ether. The combined ether extract was then extracted three times with 5-ml. portions of 0.1M sodium hydroxide solution. The combined alkaline extract was warmed to expel ether, neutralized to pH 7.0 with 1.0M hydrochloric acid, and made up to 25 ml. The solution was analyzed for phenol by the diazo method.

The results obtained are given in Table XI.

TABLE XI

RECOVERY OF PHENOL FROM AQUEOUS SOLUTION

Phenol in Original Sample, $\mu\text{g.}$	Phenol by Analysis, $\mu\text{g.}$	Recovery, %
217	188	87
27	27	100

EXTRACTION OF PHENOL FROM ALKALI CELLULOSE

The alkali cellulose was packed into a sintered glass funnel, and washed repeatedly with small portions of water until a given amount of washings had been collected. After each addition of water, a vacuum was applied to remove as much of the liquid as possible from the pad before the next addition. Efficiency of extraction was improved by incorporating a large portion of the hydrochloric acid needed to neutralize the washings into the early phase of the washing procedure. Two batch sizes of alkali cellulose were encountered in this work; a "large" batch of about 300 g. from which 1 liter of washings were collected, and a "small" batch of about 100 g. from which 400 ml. were collected.

Chloroform was used to extract phenol from the original washings because it is nonflammable and less volatile than ether. It was necessary to salt the aqueous washings with sodium chloride to obtain a favorable transfer of the phenol. Sodium chloride was added until the solution was nearly saturated; the solution was neutralized with concentrated hydrochloric acid, and made acidic to a pH of 3.0 with phosphoric acid.

Diethyl ether and chloroform can be used interchangeably to extract phenol from acidified aqueous solutions if salt is added when chloroform is used (64). In most cases, the acidified aqueous extract was given 5 extractions of either 20 or 40 ml. of chloroform, depending on the amount of aqueous extract.

The next step was to extract the ether or chloroform extract with 0.1M sodium hydroxide solution. In earlier work, this was done with 3 portions of 5 ml. each: the combined extracts were warmed, neutralized and made up to 25 ml. for phenol analysis. However, it was soon discovered that unidentified substances were present which interfered strongly with the phenol analysis. These substances

were apparently by-products of the autoxidation reaction, for this interference was very great with aged alkali cellulose samples and very low on freshly prepared alkali cellulose samples. When these solutions were made acidic (pH 3) and distilled, both phenol and interfering substance distilled over together. However, if the pH was adjusted to 8.0 and the solution distilled, the phenol distilled over, while the interfering substance remained behind.

It was necessary to extract the ether or chloroform extract with larger volumes of 0.1M sodium hydroxide solutions when this distillation step was used. When there were 200 ml. of the organic solvent to extract, 5 portions of 25 ml. each were used; when there were 100 ml. of the organic solvent, 3 portions of 20 ml. each were used. The combined alkali extracts were warmed to expel organic solvent, salted (8 or 15 g. sodium chloride were added, depending on the amount of liquid), buffered [10 or 20 ml. of pH 8.0 phosphate buffer (8%) were added, depending on the amount of liquid] and the pH was adjusted to 8.0. For a large sample, 100 ml. of the distillate was collected; for a small sample, 50 ml.

On a 243-microgram sample of phenol, a recovery of 102.7% was obtained during the application of the distillation step. This is within the error of the method.

PHENOL STABILITY IN AUTOXIDIZING ALKALI CELLULOSE

It was necessary to conduct an experiment which would demonstrate that phenol is stable in autoxidizing alkali cellulose, and would also evaluate the efficiency of the extraction procedure for phenol. Two batches of alkali cellulose were prepared: one contained phenol, the other was a blank. Half of each sample was analyzed prior to aging, the remainder after aging.

The results are summarized in Table XII.

TABLE XII

PHENOL STABILITY AND RECOVERY EXPERIMENTS

	High-level ^a	Low-level
Original amount of phenol added, $\mu\text{g./g.}$	about 60 ^b	0.30
Amount of phenol, by analysis, before aging, $\mu\text{g./g.}$	41.7	0.22
Amount of phenol, by analysis, after aging, $\mu\text{g./g.}$	23.4	0.14
Time of aging, min.	14,000	12,660
Temperature of aging, $^{\circ}\text{C.}$	30	30
Recovery, %		
Based on original added phenol	54	47
Based on initial analysis	78	63

^aFor the high-level run, the phenol was weighed approximately on an ordinary analytical balance in the solid form. It was added to the steeping liquor used in preparing the alkali cellulose. In the low-level experiment, the amount of phenol was accurately determined before it was added.

^bAll phenol weights are reported per gram of alkali cellulose.

The results reported in Table XII indicate that the recovery of phenol from aged alkali cellulose is similar on a percentage basis at the two levels studied.

APPENDIX IV

DIAZO METHOD FOR PHENOL DETERMINATION

The diazonium salt of sulfanilic acid undergoes a coupling reaction with most phenolic materials, some amines and some hydrocarbons, giving intensely colored derivatives. This has been used as a colorimetric method for determining phenol for many years (76) but there were two drawbacks to the method. First, the diazonium salt was not considered stable, and had to be prepared freshly for each day's work. Second, the coupling reaction was thought to occur only in alkaline solutions. When the mixture of phenol and diazonium salt were made alkaline, only a few minutes were available for analysis before both sample and blank darkened badly.

It was discovered that by buffering the sample at pH 7.0 the color would develop, but the darkening would not occur. The diazonium salt could be prepared in advance and kept indefinitely if stored under normal hydrochloric acid, and kept at 0 to 5°C.

PROCEDURE

Water

Ordinary distilled water is not pure enough for use in this method. Water which had been redistilled from alkaline permanganate solution was found to be free of phenol, as determined by this method. Five grams each of potassium permanganate and sodium hydroxide were added to about 3 liters of ordinary distilled water, and the solution distilled slowly. More water was added periodically, in order to keep the level to 2 liters.

Buffer

A solution of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ was prepared from 8 g. of the hydrated salt per 100 ml. solution. Using a carefully standardized pH meter, this solution was adjusted to pH 7.00 with 5N sodium hydroxide solution. It was then ready for use.

Diazotized Sulfanilic Acid Reagent

Solid p-diazobenzenesulfonic acid was prepared from either the free acid or the sodium salt of sulfanilic acid (91). The solid was collected on a sintered glass filter and washed with cold normal hydrochloric acid until it was free from highly colored impurities. When this had been done, the pale yellow solid was washed into a 125-ml. glass-stoppered Erlenmeyer flask with normal hydrochloric acid, and stored at 0 to 5°C. The supernatant solution becomes saturated with the diazotized sulfanilic acid. This solution was used as reagent. It remains usable for at least 2 months, and may be rejuvenated, as long as the solid substrate remains, merely by draining off and replacing the hydrochloric acid solution.

Analytical Procedure

If the solution to be analyzed for phenol was an alkaline extract, its pH was adjusted to 7.0 with 8.5% phosphoric acid. Two aliquots of 5 ml. each were pipetted into separate test tubes. Two reference samples of redistilled water were also prepared, in the same way. One milliliter of the 8% phosphate buffer was pipetted into each of the four test tubes. The tubes were shaken.

The absorbance of one of the samples was determined against one of the blanks before reagent was added. This value represented the absorbance of the sample not due to phenol, and was subtracted from the final absorbance. The

determinations of absorbance were made on the Beckman DU spectrophotometer, at 354 μ wavelength, and 0.13 mm. slit width.

Next, one drop of the supernatant solution of the diazotized sulfanilic acid reagent was added to each of the remaining two test tubes. The color developed slowly over a period of about 30 minutes. Readings of absorbance were taken every few minutes until a maximum was reached. The time required to reach the maximum varied considerably with the ionic content (usually sodium chloride) of the solutions and with temperature.

An absorbance versus concentration curve was constructed from standard phenol solutions (Fig. 8 and 9 and Table XIII). Resublimed phenol was used in preparing the standard solutions. Absorbance values were converted to concentration by means of these curves.

RECHECKS ON THE METHOD

Twenty days after the calibration curve had been constructed, a fresh solution of phenol was prepared, by dissolving 0.1085 g. of resublimed phenol in 1 liter of water. The concentration of phenol was 108.5 p.p.m.

The phenol concentration was determined by the diazo method at two dilutions (Table XIV).

Two months after the calibration curves had been constructed, another check was made on the diazo method (Table XV). Stock phenol solution was prepared, at 1294 p.p.m., which was further diluted for use. Old diazo reagent was used (two months old and slightly yellow) for one set of determinations; fresh diazo reagent was used for the other.

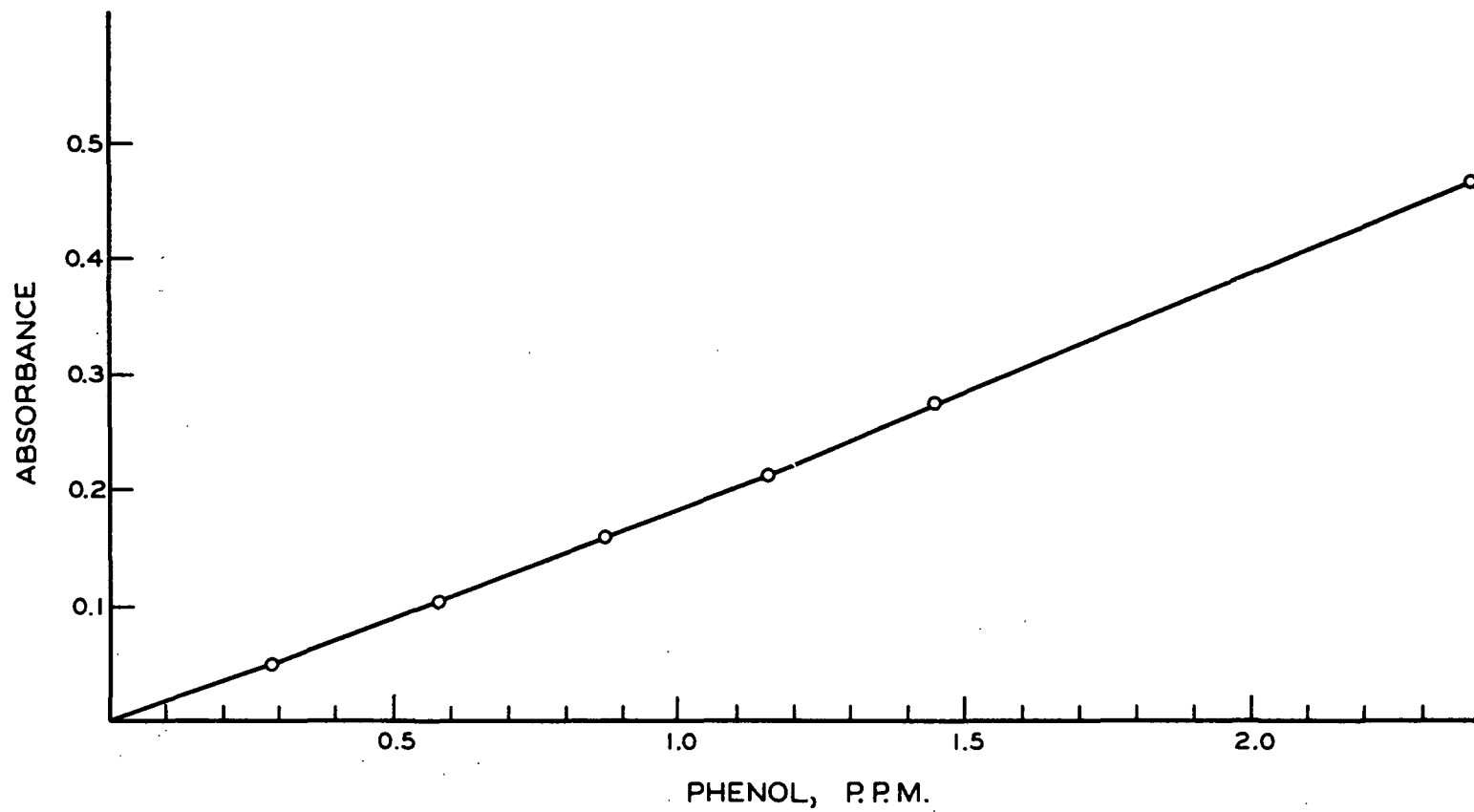


Figure 8. Phenol by Diazo Method:
Low Level

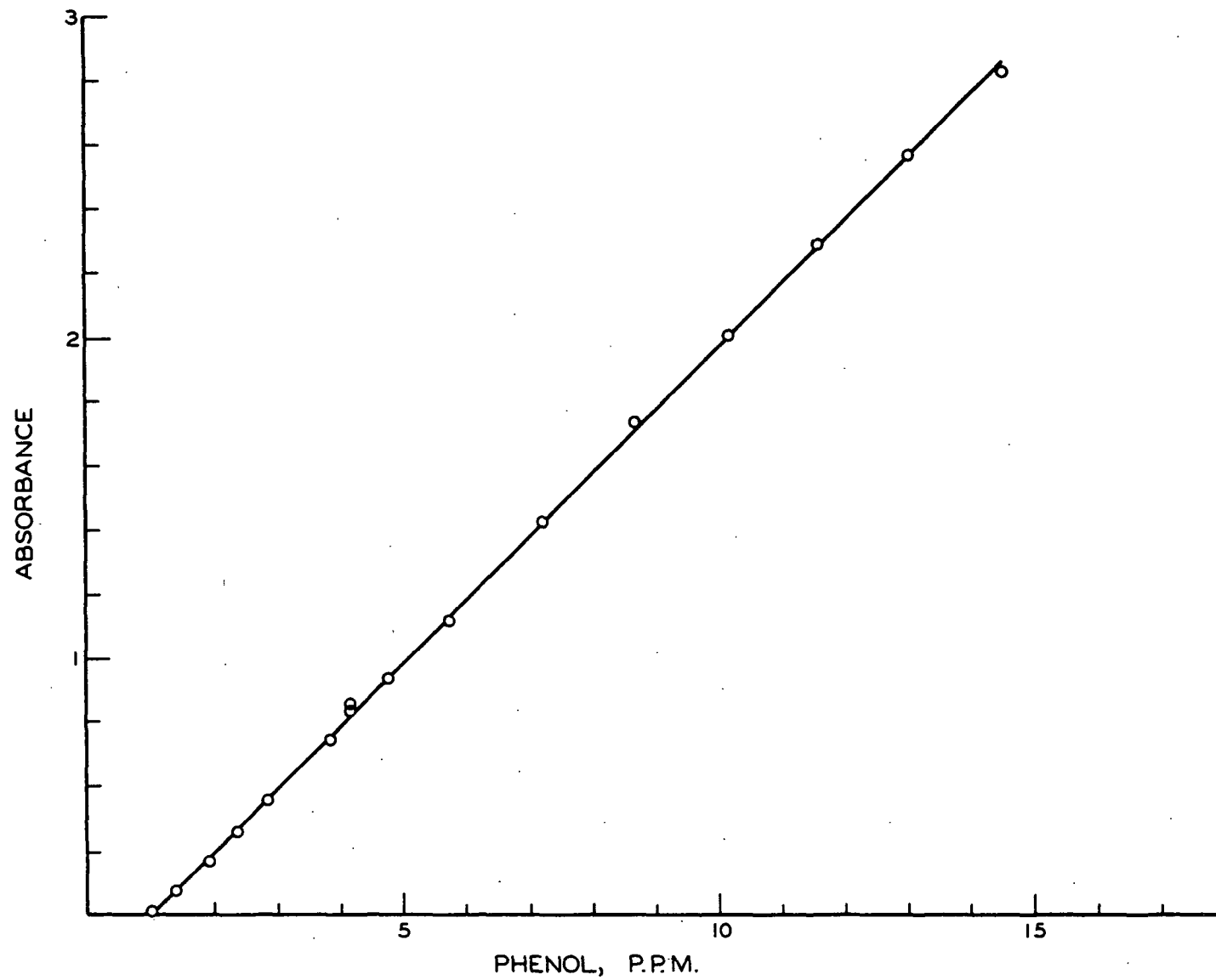


Figure 9. Phenol by Diazo Method: High Level

TABLE XIII

DATA FOR CALIBRATION CURVES

Phenol Concentration, p.p.m.	Absorbance at 354 mμ
0.289	0.050
0.579	0.103
0.868	0.158
1.158	0.212
1.447	0.273
2.38	0.462
3.81	0.751
4.14	0.838
4.14	0.855
4.76	0.939
5.79	1.17
7.24	1.40
7.24	1.40
8.68	1.73
10.13	2.00
11.58	2.28
13.00	2.56
14.47	2.82

TABLE XIV

RECHECK ON DIAZO METHOD; PHENOL ANALYSES

	Dilution of Stock	
	25:1	100:1
Trial 1, p.p.m.	4.27	1.082
Trial 2, p.p.m.	4.27	1.079
av.	4.27	1.080
Actual concn., p.p.m.	4.34	1.085
% Error	1.6	0.5

TABLE XV
RECHECK ON DIAZO METHOD; PHENOL ANALYSES

	Dilution of Stock			
	1:250		1:500	
	Reagent		Reagent	
	Old	Fresh	Old	Fresh
Measured, p.p.m.	4.98	5.00	2.43	2.50
As prepared, p.p.m.	<u>5.20</u>	<u>5.20</u>	<u>2.60</u>	<u>2.60</u>
% Error	4.2	3.8	6.5	3.9

As the phenol used in preparing the stock solution was somewhat old, it had probably picked up moisture and gave the error noted. Old reagent gave somewhat lower, but still comparable, results to fresh reagent.

APPENDIX V

ANALYSIS OF BENZENE IN ALKALI CELLULOSE

The work described in this appendix relates to the study of phenol production from benzene and autoxidizing alkali cellulose. In conducting this experiment, 5 ml. of benzene (4.4 g.) were added to the alkali cellulose at the beginning of the autoxidation period, and special precautions were taken to prevent its loss (see Fig. 1). However, it was considered advisable to demonstrate that benzene was present for the entire period of autoxidation.

The method of analyzing the alkali cellulose for benzene was as follows: The benzene was stripped out of the alkali cellulose by a stream of air, and absorbed in chloroform. The details of this can be seen in Fig. 10. A stream of air was passed slowly through the alkali cellulose, where it mixed with benzene. The air and benzene then passed through a calcium chloride drying tube to remove water, and then through the chloroform bubblers. A volume of chloroform of 75 ml. was used in each bubbler. The first bubbler was chilled with ice water; the second with a dry ice and acetone mixture.

The chloroform was removed when it was judged that the benzene transfer was complete, and made up to 100 ml. in volumetric flasks for analysis.

THE ANALYSIS OF BENZENE IN CHLOROFORM

Benzene can be analyzed directly when it is dissolved in chloroform, from its absorption of light at 255.75 μ , with the use of the Beckman DU spectrophotometer. Quartz cells were used, and the slit width was 0.9 mm. The following data (Table XVI) were taken in order to obtain the absorptivity. (Absorptivity equals the absorbance divided by the concentration of solute).

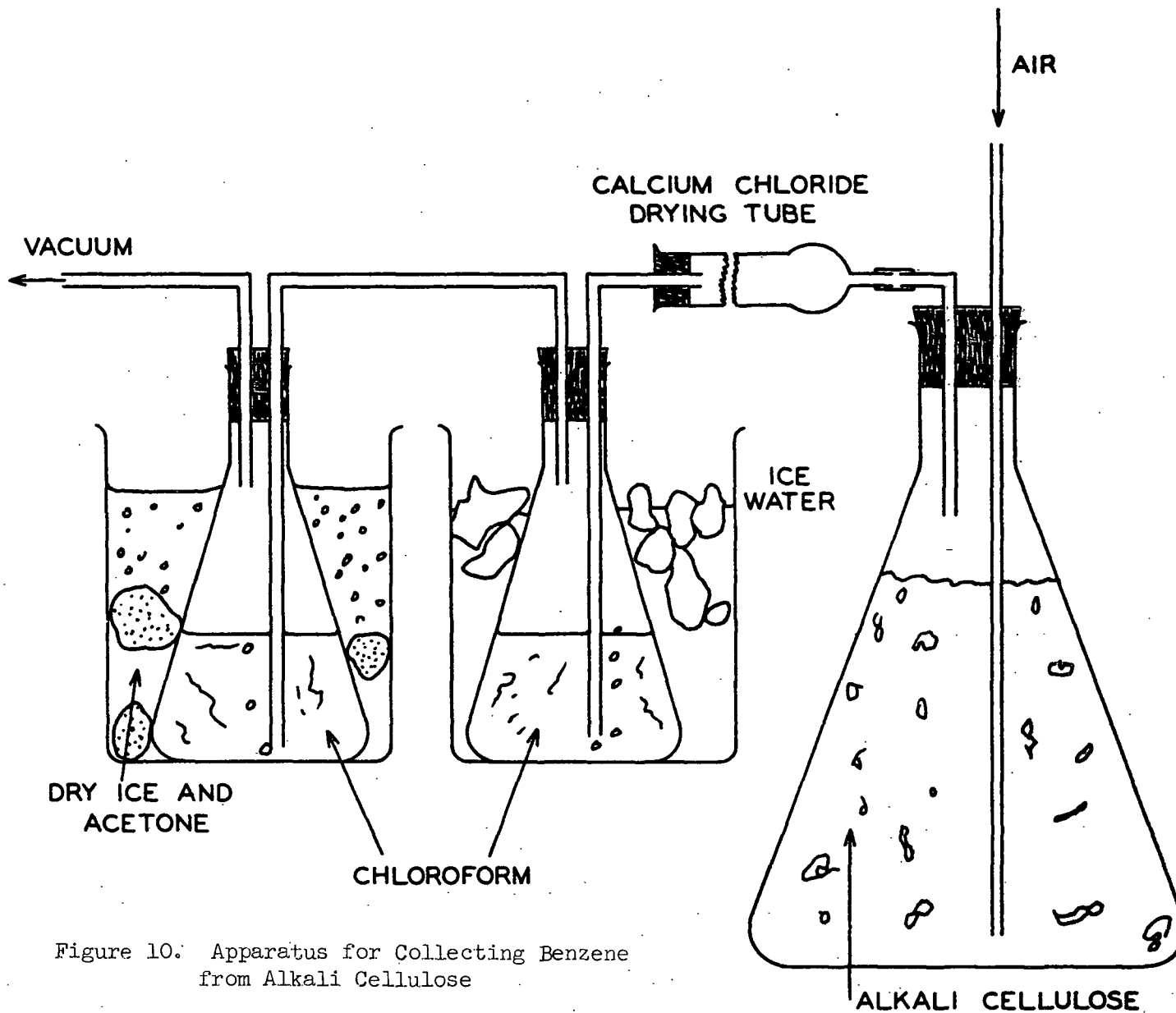


Figure 10: Apparatus for Collecting Benzene from Alkali Cellulose

TABLE XVI

ABSORBANCE OF BENZENE IN CHLOROFORM

Concn., g. Benzene/ml. $\times 10^4$ Chloroform $\times 10^4$	Absorbance
0.18	0.032
0.35	0.083
0.53	0.108
0.70	0.167
0.88	0.202
1.76	0.368
3.52	0.733
5.27	1.067
7.03	1.393
8.79	1.640

An average absorptivity of 2087 ml./g. was calculated from this data.

Two sets of trials on the method were conducted before it was used to determine benzene in the autoxidizing alkali cellulose. The first of these trials consisted of simply pipetting 1 ml. (0.879 g.) of benzene into an empty 1 liter flask and drawing air through the flask, as previously described. After only 25 ml. bubbling, 90.3 and 92.3% recovery of benzene were determined on duplicate runs. More than 90% of the benzene recovered was found in the first bubbler.

The second trial evaluated the removal of benzene from a spongy substance, much like alkali cellulose. One-hundred grams of cotton linters were mixed with 200 ml. of water, shredded, and placed in the 1 liter flask. Five ml. (4.38 g.) of benzene were pipetted into the flask before the water-cellulose was placed on top. After passing a slow stream of air through the system for 75 minutes, the chloroform in each bubbler was analyzed. At this time 44.5% of the original benzene had been recovered. The apparatus was reassembled, with fresh

chloroform, and bubbling again allowed for 75 minutes. With the additional bubbling, 22.6% more benzene was recovered. Thus, with a total bubbling time of 2.5 hours, 67.1% of the original benzene was recovered. From 90 to 95% of the recovered benzene was caught in the first bubbler.

ANALYSIS OF BENZENE IN ALKALI CELLULOSE

The alkali cellulose of Run B was analyzed for benzene by the method just described. The bubbling was allowed to run for 3 hours. The analysis for benzene gave the results shown in Table XVII.

TABLE XVII

ANALYSIS OF BENZENE IN ALKALI CELLULOSE

Flask	Benzene, g.
1	0.49
2	<u>0.06</u>
Total	0.55

Thus, there was at least 0.55 g. of benzene present in the alkali cellulose after aging.

THE SOLUBILITY OF BENZENE IN 5M SODIUM HYDROXIDE SOLUTION

The solubility of benzene in 5M sodium hydroxide solution was determined by analyzing a saturated solution of benzene in 5M sodium hydroxide for benzene.

PREPARATION OF SATURATED SOLUTION

About 50 ml. of benzene was shaken with 800 ml. of 5M sodium hydroxide in a 1 liter separatory funnel, and was allowed to stand for 24 hours in a 25°C. constant temperature room. Portions of the clear aqueous phase were drawn off and extracted with cyclohexane.

EXTRACTION PROCEDURE

A 250-ml. separatory funnel was fitted with a teflon stopcock. Twenty-five milliliters of spectrographic-grade cyclohexane were placed in the separatory funnel, and it was tared. About 150 ml. of the 5M sodium hydroxide saturated with benzene were added, and it was reweighed. Three successive extractions with cyclohexane of 25 ml. each were carried out. The cyclohexane extract was diluted to 100 ml., and analyzed for benzene by spectrophotometry at 255.5 millimicrons.

CALIBRATION CURVE OF BENZENE IN CYCLOHEXANE

Benzene in cyclohexane was determined by the absorbance of light at 255.5 μ on the Beckman D.U. spectrophotometer. Quartz cells were used, and a slit width of 0.92 mm. employed. The data in Table XVIII show a slight deviation from Beer's law, and graphical interpolation was used.

TABLE XVIII
ABSORBANCE OF BENZENE IN CYCLOHEXANE

Conc., g. benzene/ml. of cyclohexane, $\times 10^4$	Absorbance
1.76	0.345
1.76	0.364
3.52	0.664
3.52	0.673
5.27	0.979
5.27	0.979
7.03	1.200
7.03	1.220
8.79	1.422
8.79	1.435

RESULTS OF SOLUBILITY DETERMINATIONS

Table XIX gives the results of the solubility determinations for benzene in 5M sodium hydroxide.

TABLE XIX

SOLUBILITY OF BENZENE IN 5M SODIUM HYDROXIDE

Trial	Wt. NaOH Soln., g.	Wt. Benzene, g.	Parts Per Million
1	171.94	0.0107	62.3
2	173.57	0.0102	58.8
3	258.38	0.0158	61.3
Average			60.8
Rounded Average			61